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by

Bryant Mather

November 1964

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U. S. Army Engineer Waterways Experiment Station
CORPS OF ENGINEERS
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PREFACE

This paper was prepared in accordance with a request contained in a multiple letter dated 23 September 1964, subject, "Agenda for 1964 Division Laboratories' Conference," from the Division Engineer, U. S. Army Engineer Division, New England. Two of the subjects proposed by the U. S. Army Engineer Waterways Experiment Station (WES) for discussion were selected for inclusion as 10-minute papers in sessions scheduled to be held on 18 November 1964. It was requested that 50 copies of each of these papers be made available for distribution at that time.

The paper was prepared at the Concrete Division, WES, under the direction of Mr. Thomas B. Kennedy. The Director of the WES during the preparation of the paper was Col. Alex G. Sutton, Jr. CE. Technical Director was Mr. J. B. Tiffany.

Alkali Reactions with Carbonate Rocks*

by
Bryant Mather**

ABSTRACT

The chemical reactions of "dedolomitization":

1. $CaMg(CO_3)_2 + 2(Na, K)OH \longrightarrow Mg(OH)_2 + CaCO_3 + (Na, K)_2CO_3$
   (dolomite) (alkali) (brucite) (calcite) (alkali carbonate)

2. $(Na, K)_2CO_3 + Ca(OH)_2 \longrightarrow 2(Na, K)OH + CaCO_3$
   (alkali carbonate) (calcium hydroxide) (alkali) (calcite)

indicate how dolomite can be altered to brucite and calcite and how the alkali can be regenerated by reaction with calcium hydroxide.

Other chemical reactions involving alkalies and carbonate rocks are less well understood but involve solution and redeposition of calcite and silica with the production of zoning and "rimming" of carbonate rock aggregate particles.

Work at USAEWES (CD) has revealed that dedolomitization occurs with dolomite in sand from Watertown, South Dakota (WES MP 6-530, Sep 1962), and dolomite from the Chickamauga formation as used by TVA in Chickamauga Dam (WES TR 6-637, Dec 1963). A variety of zoning and rimming, some involving rocks with no dolomite, was found in concrete from structures in Kansas and Nebraska (WES TR 6-629, June 1963).

A symposium containing 14 contributions was held at the 1964 Highway Research Board meeting, the results of which will be published in 1964. As part of ES 603, WES (CD) is making expansion tests of numerous carbonate-rock prisms including a series from rocks from the Huntington District that may, in part, be related to rocks shown to be reactive by work of the Virginia Department of Highways. A procedure for making such tests is being developed.

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*Prepared for presentation at 1964 CE Division Laboratories' Conference, 18 November 1964, Boston, Massachusetts.

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Introduction

Until relatively recently the term "alkali-aggregate reaction" was understood to refer to either a single reaction -- that of alkalies (sodium or potassium or both) with soluble silica in aggregates -- or a variety of reactions, all of which involved silica as the reactant derived from the aggregate. This rather simple understanding began to be undermined by a variety of sorts of reported results beginning at least as far back as 1953 when Katharine Mather reported[1] that certain limestone aggregates containing about 4 percent of a swelling montmorillonite clay, crushed to sand size, and stored in synthetic sea water expanded 2.3 percent of the original dry volume more than similar samples stored in tap water and 2.8 percent of the original dry volume more than similar samples stored in calcium hydroxide solution. This suggested a chemical role for alkalies in concrete durability in cases in which the aggregate was carbonate rock.

In 1957 Swenson and his associates began to report[2] on the behavior of concrete in the Kingston, Ontario, area.

In 1958 Lemish and associates began to report[3] on the behavior of concrete and aggregates from Iowa.

In 1961 Hadley presented[4] the first coherent picture of the probable chemical reactions and an hypothesis relating these to physical consequences. It is to his work that we owe the small rock prism test for expansion after storage in sodium hydroxide; the introduction of the dedolomitization reaction as a fundamental chemical process in at least some of these phenomena; and the suggestion that rocks capable of participation in dedolomitization need to meet multiple criteria. The various criteria were suggested to be (1) calcite:dolomite ratio (near 1:1), (2) acid-insoluble residue (range 10 - 20%), (3) clay mineralogy (dominantly clay mica ("illite")), and (4) texture (dolomite rhombs in a fine calcitic matrix).

By 1962, carbonate-rock reaction was generally recognized as a significant phenomenon in concrete durability, and a section was devoted to it in the report, "Durability of Concrete in Service," prepared by ACI Committee 201.[5]

At about this same time the occurrence of expansion of concrete due to alkali-carbonate rock reaction in Virginia was reported by Newlon and his associates.

CE Work

In the May 1960 Summary of Pertinent Activities at Division Laboratories and in the report of the Eighth Division Laboratories' Conference (Nov 1960)

mention is made of MRDL work on sands from Watertown, S. D. The observations reported were of interest to Mrs. Mather, who had been following the informal reports that she had received from Swenson, Lemish, and Hadley and also because it was suggested by MRDL that the active factor in the aggregate might be montmorillonite clay as had been found to be the case in her previous work.[1] As a result, through the cooperation of MRDL, certain samples were obtained for study at WES-CD by her and A. D. Buck. The results of this study appeared in September 1962.[7] It was found that the montmorillonite contained low cristobalite-tridymite which participated in alkali-silica reaction, and also that dolomite particles had undergone dedolomitization. This study is the first of which record is available in which the brucite ($Mg(OH)_2$) postulated by Hadley[4] as the product of the dedolomitization reaction was actually found to be present and identified by X-ray diffraction.

A second investigation, begun in 1961, of concrete cores from Kansas also revealed evidence of alkali-carbonate rock reaction.[8] The results of this study and those of the previous one were summarized in a paper prepared for and presented as part of a Symposium on Carbonate Rock Reaction sponsored by HRB Committee MC-B2 at the January 1964 HRB Meeting. The publication of this symposium has been delayed but the volume should be available before 1 January 1965. The paper on the WES work is entitled "Alkali-silica and Alkali-carbonate Reactivity of Some Aggregates from South Dakota, Kansas, and Missouri," by Katharine Mather, Alan D. Buck, and Wilbur I. Luke.

Meanwhile in October 1962 the Tennessee Valley Authority approached the USAEWES for aid in developing data that might assist in explaining expansion of concrete that had caused trouble in Unit 3 of the powerhouse at Chickamauga Dam. A study of cores from the affected structure revealed evidence of dedolomitization. The results have been reported by W. I. Luke in a WES Technical Report[9] and will be mentioned briefly in a discussion of a paper in the HRB Symposium, since it has been noted that the rocks involved may be stratigraphically correlated with some in Virginia found to be reactive by Newlon and Sherwood. A paper on this work is in press for the 1964 Proceedings of ASTM.

Having traced alkali-carbonate reaction involving dedolomitization by stratigraphic correlation from western Virginia to southeast Tennessee, it is only prudent to assume the likelihood that it is potentially encounterable in other areas stratigraphcally and lithologically related to these. Thus, when CCE noted interest by the Huntington District in quarries containing such rocks, it directed ORD to have Huntington send samples to WES-CD for study. These tests are in progress. Some samples have expanded significantly due to storage in NaOH.

Some of the rocks showing evidence of chemical reaction in the cores studied for Milford Dam[8] were, surprisingly, found to be purely calcitic limestones -- containing no dolomite whatsoever -- as indicated by X-ray diffraction. The chemical reactions of these rocks were not clearly detrimental and were not specifically identifiable as dedolomitization. The

nature of these reactions was under study during the period September 1963 - September 1964 at Purdue University by Alan D. Buck as his research project while holding a Secretary of the Army's Research and Study Fellowship and completing the requirements for a master's degree. Mr. Buck's thesis will be published in the near future.

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