REACTION PRODUCTS IN EXPANSION TEST SPECIMENS OF CARBONATE AGGREGATE

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Detailed petrographic examinations and X-ray diffraction analyses were made of carbonate aggregates that had been tested by ASTM Methods C 227 and C 586. It was found that the most expansive mortar bars exhibited more external cracks and deposits of reaction products than did the less expansive bars. Any reaction rims were within the aggregate particles, and etching with various strengths of hydrochloric acid showed that they were negative. Rim-forming aggregates within the mortar bars appear in thin section to have undergone dedolomitization in the rim zone at the paste-aggregate interface. X-ray examination of the most expansive aggregates from these mortar bars failed to detect any brucite. However, comparison of the diffractograms generated by X-ray reflection from these reacted aggregates with diffractograms generated by the fresh, unused portions of these aggregates indicated that some type of dedolomitization reaction had occurred. The information obtained indicates that, under conditions found when testing rock for expansion by ASTM C 586, the minerals of the hydrotalcite-sjogrenite mineral groups (complex magnesium carbonate hydroxides) can be the chief products of alkali dedolomitization near the surface of the test prisms of dolomite carbonate aggregate and that brucite can be the major dedolomitization product in the interior of the aggregate.

•THE petrographic examinations described in this paper were made on samples used in a broad research program of the Virginia Highway Research Council (1). This program included studies designed to assess the ability of various test methods to detect detrimental reactions between aggregates and alkalies (2). The test methods studied included ASTM C 586 for rock prisms, ASTM C 227 for mortar bars, ASTM C 157 for concrete beams, and petrographic examinations by ASTM C 295.

Concurrently with this broad study of various test methods, the Council cooperated with the subcommittee on chemical reactions of the ASTM committee on concrete and concrete aggregates in an interlaboratory study of Method C 227 by four agencies. The purpose of this interlaboratory study was to determine the applicability of the mortar bar method to the detection of expansion caused by alkali-carbonate reactions. The results of expansion tests on specimens exposed for 6 months were reported by the four cooperating agencies in 1965 (3). A report on a portion of the study (including some petrographic examinations) conducted by the Waterways Experiment Station was submitted to the ASTM subcommittee in 1966 (4). This report included expansion results at 19 months. The major findings from the ASTM studies were summarized by Newlon (2). The petrographic examinations were made to identify products of the reactions between carbonate aggregate and alkalies in the hope that the mechanisms of alkali-carbonate reaction and expansion could be better understood.

SAMPLES

In the cooperative testing program, 5 of the 22 aggregates from the Council's broad research program were studied along with 2 aggregates submitted by the

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Waterways Experiment Station, K-4 G-6 (3) and OM-16 G-1 (2). The details of the sampling for the Virginia aggregates have been given by Newlon et al. (1).

The 7 aggregates used and the percentage of expansion of the mortar bars and prisms are given in Table 1. The mortar bars had been made as part of the cooperative interlaboratory study of Method C 227 and tested in accordance with that method. The bars studied were those that had been made with high-alkali cement (Na_2O equivalent = 0.95 percent). The only aggregates that had produced significantly expanding mortar bars were 27-4, 12-9, and 1-8. The study of these 3 aggregates included petrographic examinations of matching prisms that had been tested under Method C 586.

The prisms of aggregates 27-4 and 12-9 had been shaped from pieces of the same samples of aggregates that had been used in the cooperative mortar bar testing program. In most cases the original pieces of rock from which the prisms had been cut were still available for comparison. The prisms of 1-8 had been cut from samples collected a year later than the aggregate used in the mortar bar study. The samples had been carefully chosen from the same quarry and lithologic unit, and every attempt had been made to duplicate the original 1-8 sample. The lithologic unit 1-8 is quite homogeneous; it has little variation in texture, color, or mineralogic composition.

Table 1. Samples examined for reaction products formed by the testing of aggregates for expansion due to alkali-carbonate reaction.

	Mortar Bars Examined[b]		Prisms Examined[c]			
Aggregate[a]	Percent Expansion	Months of Storage	Number of Prisms	Percent Expansion	Weeks of Storage	Remarks
27-4	0.128	25				Significant expansion, very faint rims
			2	1.92	200	Calcite dolomite
				0.100	200	Slightly dolomitic limestone
12-9	0.144	25				Significant expansion, rims visible on polished slabs
			2	4.986	200	Dolomitic limestone
				2.793	52	Dolomitic limestone
				Broke after 52 weeks		
29-5	0.056	25	None			Dolomitic limestone
36-X	0.064	25	None			Slightly dolomitic limestone
1-8	0.118	25				Significant expansion, no rims detectable on typical material
			7	0.862	36	Impure dolomitic limestone, dolomite content usually equal to calcite content
				Too long to measure at 40 weeks		
				1.958	180	
				1.038	167	
				0.709	167	
				1.073	167	
				1.087	167	
				0.887	167	
K-4 G-6 (3)	0.055	20	None			Rims very definite, micrite limestone
OM-16 G-1 (2)	0.076	20	None			Rims definite, cherty dolomitic limestone

[a]Throughout the Virginia research, a 2-digit designation has been used to identify sources; the first indicates a specific quarry and the second a specific lithology. Thus "1-8" indicates a sample from quarry 1 and lithology 8.
[b]Had been tested for expansion by moist storage.
[c]Had been tested for expansion by storage in NaOH.

PROCEDURES

The mortar bars were examined megascopically and microscopically on exterior surfaces, fractured surfaces, cut and polished surfaces, and surfaces that had been polished and etched. Thin sections of the mortar bars and of aggregate particles from them were examined with a polarizing microscope, and particles of the aggregate were removed from the mortar bars and analyzed by X-ray diffraction procedures.

The rock prisms that had been used for expansion testing were examined in thin sections with the polarizing microscope and compared with thin sections made of the original samples from which the prisms had been cut.

One surface each of 2 tested rock prisms of each expansive aggregate was scanned with the X-ray diffractometer; an increment of thickness was ground from the surface, and the prism was scanned again. The procedure was repeated 10 times for each 27-4 prism, 7 times for each 12-9 prism, and 16 times for each 1-8 prism. In addition, one surface each of 4 additional prisms of aggregate 1-8 was scanned with the diffractometer to facilitate a detailed study of surface components. The surfaces of another prism of aggregate 1-8 were scraped in 6 very small increments until a depth of 0.001 in. (25 μm) was removed from each side. The prisms and the scrapings were subjected to analysis by X-ray diffraction between each removal of material.

Samples of the original untreated aggregate were analyzed by X-ray diffraction.

Diffraction patterns were generated of the crystallized residue of the liquid in which the prisms had been stored.

RESULTS

Mortar Bars

Portlandite crystals and ettringite crystals were found on the surfaces and/or in the voids of all the mortar bars. Fine-grained deposits of a mixture of calcium hydroxide, sodium-calcium carbonate, and a gel-like material were found on the surfaces of all the bars. They were best developed on the bars made with aggregates 27-4 and 1-8 and least common on those made with 29-5, 36-X, and K-4 G-6 (3).

A minor amount of very fine cracks were found on the finished surfaces of the most expansive mortar bars—those containing aggregates 27-4, 12-9, and 1-8. No cracks were observed on the bars made with aggregates 29-5, 36-X, and K-4 G-6 (3).

Negative reaction rims within the aggregate were common in the mortar bars made with K-4 G-6 (3) and OM-16 G-1 (2). These rims were easily observed on etched and polished slabs of the mortar bars. Negative rims were detected only with difficulty within the aggregate particles of the mortar bar made with 12-9. A trace of rims similar to those observed on aggregate 12-9 was found on a few aggregate particles of the mortar bar made with 27-4.

Peripheral expansion cracking was easily seen on the polished surfaces of the mortar bar made with aggregate 12-9. Many of the aggregate fragments showed a narrow, dark reaction rim. Frequently a fine, white crack paralleled the reaction rim just inside it (Figure 1). Peripheral expansion cracking in carbonate aggregate is usually considered to be definite evidence of expansive alkali-carbonate reactivity. Rimmed particles of aggregate 12-9 also showed cracks that traversed the length of elongated fragments and random cracks in several directions across the more equant pieces. A few of these cracks within the aggregate were traced through the paste to the surface of the mortar bar, where they could be seen on the finished surfaces. The peripheral, random, and longitudinal expansion cracking of the aggregate is, therefore, thought to be the cause of the external cracks noted.

Aggregate 27-4 showed slight evidence of peripheral expansion cracking. No other evidence of peripheral expansion cracking was found in the aggregates of any other mortar bar.

Aggregate 1-8 exhibited a few fine, white cracks that curved across the aggregate fragment and may well have been due to expansion of the aggregate particles. Cracks of this type have been noted frequently in particles of 1-8 aggregate in concrete that has expanded in service.

Figure 1. Expansion cracking—peripheral and random—in aggregate 12-9 mortar bar.

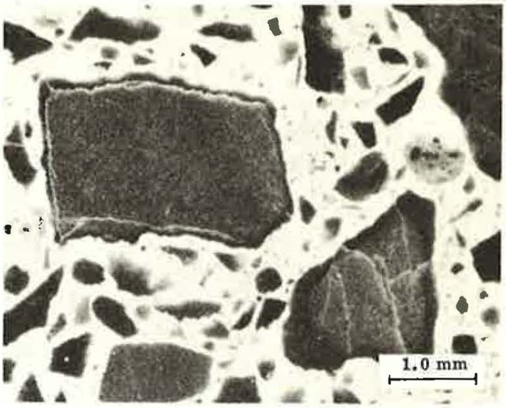


Table 2. Dolomite to calcite peaks: original samples of aggregate versus aggregate removed from mortar bars.

	Ratio of Dolomite/ Calcite Peak Heights	
Aggregate	Original Sample	After Use in Mortar Bars
27-4	1.5[a]	0.75
12-9	0.66	0.15
1-8	1.5	1.00

[a]The original aggregate 27-4 was extremely variable in composition and the ratio listed here is an average of several ratios obtained from diffractograms generated by the several types.

Figure 2. Rhombs of dolomite in thin section of 27-4 prism that show alteration of rhomb edges to fine-grained, unoriented calcite: partially crossed nicols.

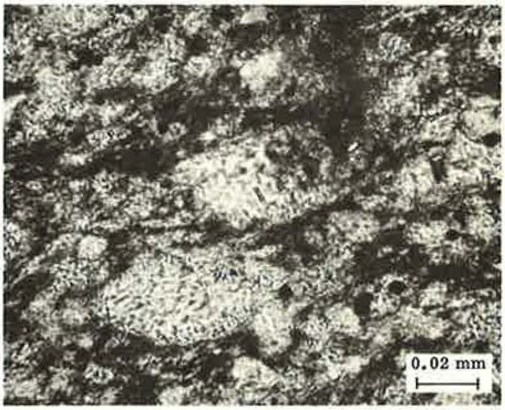
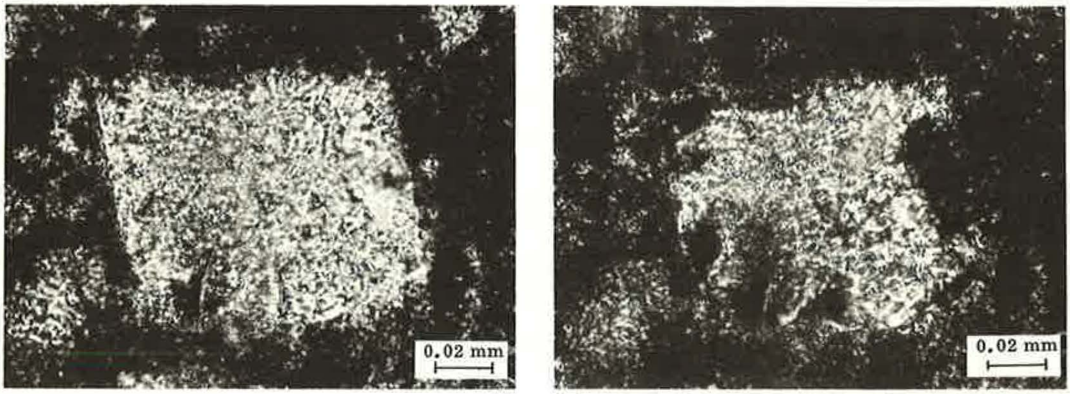


Figure 3. Large embayed rhomb of dolomite in thin section cut from prism of 1-8.



Examination of the thin sections of the mortar bars did not reveal any additional evidence that an expansive alkali-carbonate reaction had taken place. The only rims detectable in thin section were those of OM-16 G-1 (2). The innermost portion of the rim was the darkest. At the contact with the paste the aggregate particle was usually lighter in color than even the center of the particle. The rhombs of dolomite found in the outermost clarified zone of the rims exhibited an indefinite, concentric zonal structure and a wavy extinction. Wavy extinction and zoning were not present on the dolomite rhombs in the center of the aggregate particles. The aggregate apparently had undergone dedolomitization at the paste-aggregate interface.

X-ray diffraction analyses of the aggregate removed from the mortar bars were compared with diffraction analyses of the original aggregate samples, and it was seen that the dolomite-to-calcite ratio within each sample was noticeably less in the treated material than it was in the unused portion of the aggregate. The ratios are given in Table 2. No brucite was detectable in any of the samples. Despite the absence of brucite, the dolomite/calcite ratio changes indicated that a dedolomitization reaction had occurred.

Prisms

It was noted during the production of the thin sections of the prisms that had been tested by storage in NaOH that the prisms were softer and more easily ground away than were the original rock samples from which they had been cut. The surfaces of the prisms were porous, browner in color, and the details of the rock fabric were obscured.

The dolomite rhombs found in the original samples were shown in the thin sections of the expansive prisms to have been altered by the action of the NaOH. The rhomb areas often showed a wavy extinction and a zonal structure similar to that found in the reaction rims of aggregate OM-16 G-1 (2) in the mortar bars. A prism of aggregate 27-4 contained numerous rhombs of dolomite in which the outer edge of the rhomb had been altered to fine-grained, unoriented calcite (Figure 2).

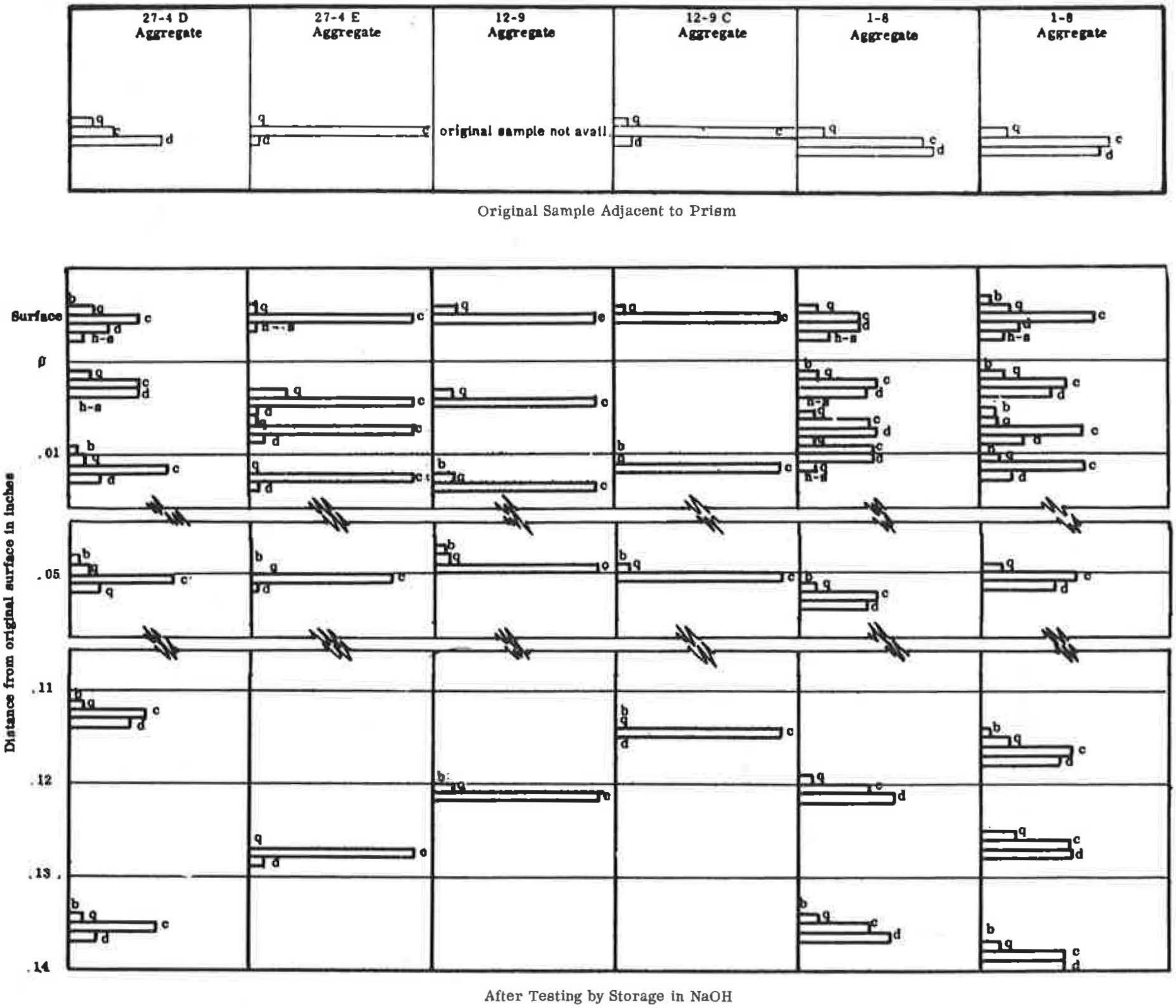
The thin section cut from the original sample of aggregate 12-9 contained a few scattered dolomite rhombs. The thin section made of the tested prism, which had been fashioned out of that sample no more than ¼ in. away, contained almost no dolomite but did exhibit rhomb-shaped holes where the dolomite had been. These rhomb-shaped voids may have contained a soft, fragile reaction product that was washed or abraded away during the production of the section. The few crystals of dolomite remaining in the prism showed a definite alteration at the edges. Prisms of aggregate 1-8 contained rhombs of dolomite with embayed edges (Figure 3).

Except for calcite, no products of the alteration of these dolomite rhombs were observed in any of the thin sections of the prisms. They may have been present interstitially in the fine-grained unoriented calcite rims or in the clay-like material occurring in the micrite matrix.

None of the thin sections made of portions of the original samples that had been immediately adjacent to the prisms showed any evidences of dedolomitization.

X-ray diffraction analyses of the surface of the tested prisms were compared with similar analyses of slabs of the original rock chunks that had been adjacent to the original prism location. Figure 4 shows the results of these analyses and the analyses of the surfaces produced by successively deeper grinding. It can be seen that the relative amounts of calcite and dolomite in the prisms were changed by the action of the NaOH. In all cases the dolomite was less abundant in the prism surface than in the original rock. Brucite was only rarely found at the surface and then in only small quantities. Four of the prisms (2 of 27-4 and 2 of 1-8) had surface reaction products that gave a broad, moderately strong reflection at 7.7 to 7.9 Å that often consisted of two recognizable peaks. No other peaks of unknown origin were clearly recognizable in scans of up to 45 deg. When the surface of the prisms was ground to a depth of 0.01 in., the 7.7 to 7.9 Å reflection was no longer present in the diffractograms. The substance causing the reflection was particularly abundant in the surface of prisms of aggregate 1-8. It was also present in small quantities in the surfaces of 12-9 prisms.

Figure 4. Change in composition with depth within the prisms.



Length of bar indicates relative height of major diffraction reflection of mineral indicated. Where there is no bar, letter indicates trace observed. Exception for surface patterns, calcite bar placed at depth at which diffractogram was generated.

b = brucite c = calcite h - s = hydrotalcite-sjogrenite mineral groups
q = quartz d = dolomite

Note: Lack of space precluded illustration of all surficial diffractograms generated of these prisms.

Five prisms of 1-8 were selected to facilitate study of this substance. X-ray diffractograms generated from the surfaces of these prisms confirmed the fact that the material with a reflection of 7.7 to 7.9 Å is frequently found in the exterior portion of prisms of 1-8 that have soaked for a long time in 1N NaOH solution. The outer 0.001 in. of one prism of aggregate 1-8 was investigated in 7 successively deeper increments. The traces of the diffractograms are shown in Figure 5. An inverse relationship may be seen between the concentration of the reaction product and the concentration of dolomite.

A composite sample of the scrapings from this prism was diluted with carbon black and burned in a visual, AC arc, grating-type spectroscope. Because of the small size of the sample the burn-off was very rapid and it was impossible to scan the entire spectrum and make a complete qualitative analysis. However, the splutter shown by the material indicated the presence of water, and it was possible to detect significant amounts of magnesium.

The information obtained from the diffraction charts was insufficient to allow a positive identification of the reaction product. When the presence of magnesium and hydroxyl groups was considered in conjunction with the original rock chemistry, the most likely cause of the diffraction peak at 7.7 to 7.9 Å was indicated to be substances of the hydrotalcite-sjogrenite mineral groups, brugnatellite, $Mg_6FeCO_3(OH)_{13} \cdot 4\,H_2O$, and/or pyroaurite, $Mg_6Fe_2CO_3(OH)_{16} \cdot 4\,H_2O$ (5, 6, 7, 8, 9, 10). If the clay minerals were broken down by the action of the hydroxide, 2 other minerals probably formed and probably contributed to this reflection. They are hydrotalcite and manasseite, both with the formula $Mg_6Al_2CO_3(OH)_{16} \cdot 4\,H_2O$. Because the reflection at 7.7 to 7.9 Å was broad and often consisted of two recognizable peaks, it is felt that all of these minerals may have been present.

The second strongest line expected to be produced by the minerals of the hydrotalcite-sjogrenite mineral groups is very near the calcite line at 3.86 Å. There is a definite broadening of this calcite line when the line at 7.7 to 7.9 Å is at the maximum intensity observed. This second strongest line is rather indefinite. Its presence could not be observed on diffractograms generated after the outermost surface of the prism was removed. Most of the scans did not cover the arc that includes the next strongest reflections expected. The intensities of the first 2 peaks were so low that additional peaks probably would be undetectable.

The minerals of the hydrotalcite-sjogrenite groups are closely related chemically and are in the hexagonal and rhombohedral crystal systems. They are commonly found in parallel intergrowths with each other and with brucite. They are an isostructural, polymorphous series that is probably related to the brucite group (5, 6, 7, 8).

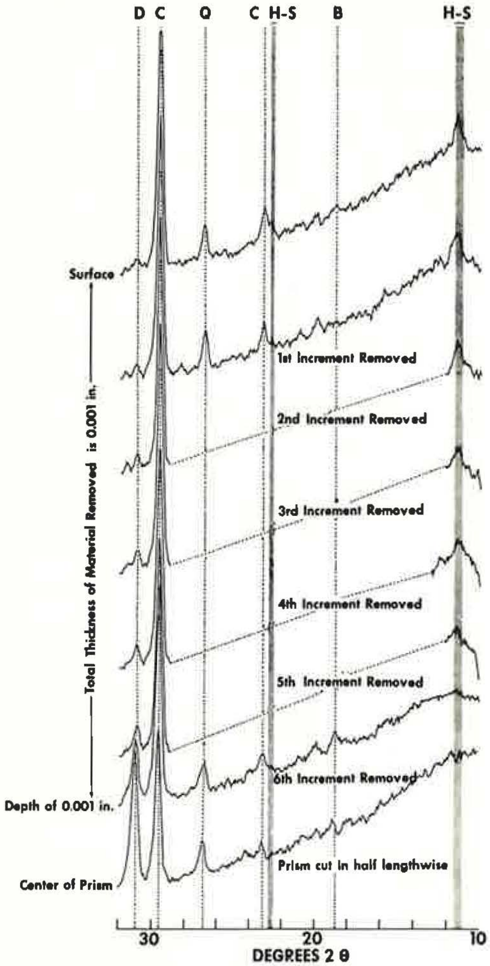
The complex carbonate hydroxide minerals have been found at the surfaces of prisms of dolomitic rocks that have been immersed in a solution of sodium hydroxide. In all cases the dolomite associated with them has been found to be less abundant than it was in the rock before it was so treated. They are apparently a reaction product of the dolomite. Brucite was present in at least trace amounts in all the dolomitic expansive prisms.

There was no apparent relationship between the amount of brucite and the depth within the prism except that the brucite was rare, especially on the surface. There was no relationship between the amount of brucite and the amount of dolomite, nor could the percent of expansion be directly related to the presence and abundance of brucite or the hydrotalcite-sjogrenite minerals. Neither the brucite nor the hydrotalcite-sjogrenite minerals occurred in the untreated samples.

Residue in Bottles Used to Store the Prisms in NaOH

The liquid in the bottles containing some of the older prisms had evaporated and carbonated, leaving a white crystalline residue. Part of this material was light and fluffy, part in needle-like crystals, and part in tabular crystals adhering to the prisms. Diffraction patterns of these substances were generated.

Figure 5. Traces of selected diffractograms produced by X-ray scan of the surfaces of prism 1-8.



D	= Expected position of dolomite reflection, 2.88 Å "d" spacing
C	= Expected positions of calcite reflections, 3.86 Å and 3.04 Å "d" spacings
Q	= Expected position of quartz reflection, 3.34 Å "d" spacing
B	= Expected position of brucite reflection, 4.77 Å "d" spacing
H-S	= Expected positions of the reflections of the minerals of the hydrotalcite-sjogrenite groups, 7.69 - 7.93 Å and 3.88 - 3.96 Å "d" spacings

Note: Continuous scans not obtained for all the interior surfaces.

No material containing magnesium was detected, and the only definite evidence found of a reaction between the sample and the solution was a minor amount of gaylussite adhering to the prism. Minor calcite may have been present in the residue, but the sodium bicarbonate pattern obscured the calcium carbonate reflections.

FURTHER RESEARCH

More study of the reactions is needed. A method of collecting a purer and larger sample of the hydrotalcite-sjogrenite minerals should be devised so that more complete X-ray diffraction data, spectrographic analyses, and optical determinations can be obtained. Comparison with standard samples available at the Smithsonian Institution may bring a more positive identification and better understanding of the importance of these phases.

A more thorough study of the reacted surfaces and rims found on the aggregates in mortar bars and concretes should be made to ascertain whether the complex carbonate hydroxides are formed by cement alkali reaction as they are in the standard alkaline test solution.

It must not be forgotten that the rocks from which these prisms and the mortar bar aggregates were obtained are the product of natural deposition and natural organic and inorganic chemical changes. Such processes never occur uniformly throughout, but rather produce a rock that is not homogeneous but patchy in texture and composition. Therefore, it is felt that the true nature and importance of these reaction products will be ascertained only after a detailed analysis of data obtained from many more samples than were involved in this study.

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