

PETROGRAPHIC EXAMINATION OF CARBONATE
AGGREGATE PRISM SPECIMENS TREATED WITH
CHEMICAL SOLUTIONS NORMALLY OCCURRING
IN PORTLAND CEMENT CONCRETE

by

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(The opinions, findings, and conclusions expressed in this
report are those of the author and not necessarily those of
the sponsoring agencies.)

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SUMMARY

The original rock prism specimens were prepared and the early length change data were taken as part of a Federal Highway Administration project on the behavior of carbonate aggregates in concrete. It had been shown that the length changes of the aggregates bore a direct relationship to the pH of the solution in which they were tested. The present study shows that the chemical reactions causing the length changes can be detected in the prisms by quantitative measurements of the mineral composition by means of X-ray diffraction and by examination of thin sections under a petrographic microscope. It is concluded that chemical solutions of pH over 12 can cause expansion and dedolomitization in carbonate rocks susceptible to alkali reactions and that chemical solutions of low pH may cause dissolution of carbonate rocks and shrinkage. It is noted that detailed, statistically defensible conclusions regarding the exact nature of the reactions occurring between the chemicals of concrete paste and the carbonate aggregates therein will probably require that data be obtained from replicate reactions and that weight changes as well as length changes be measured.

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INTRODUCTION

In 1962 Yuan-Ning Liu investigated the length changes of 1/4" x 1/4" x 1 1/4" prisms made from two carbonate aggregates and stored in LM solutions of the various soluble chemicals occurring in portland cement concrete.⁽¹⁾ This work was related to extensive studies of the behavior of carbonate aggregates in concrete being carried on at the Virginia Highway Research Council by Newlon, Sherwood, Ozol, Walker, and others. Liu compiled the results available after six weeks of tests. Newlon and Clemeña analysed the results available at 52 weeks of tests.⁽²⁾ In both cases, it was shown that the length changes of the aggregates bore a direct relationship to the pH of the solution in which they were tested, Figure 1. Hadley has shown that for Kingston alkali reactive carbonates "both the rate of expansion and the total expansion are a function of the alkali ion present" in solution.⁽³⁾ The present study compares the presently detectable chemical and textural changes in the specimens prepared by Liu with the length changes at 13 months and the chemical species present in solution.

SAMPLES

Forty prisms had been stored by Liu individually in polyethylene bottles. During the course of several years the water of the chemical solution evaporated and the solutions crystallized. Three of the prisms had been removed for use in other studies and two had completely dissolved. The prisms available, the length changes, the chemicals used, and the appearance of the prisms after rinsing in distilled water are listed in Table 1 in order of decreasing chemical pH of the soaking solutions.

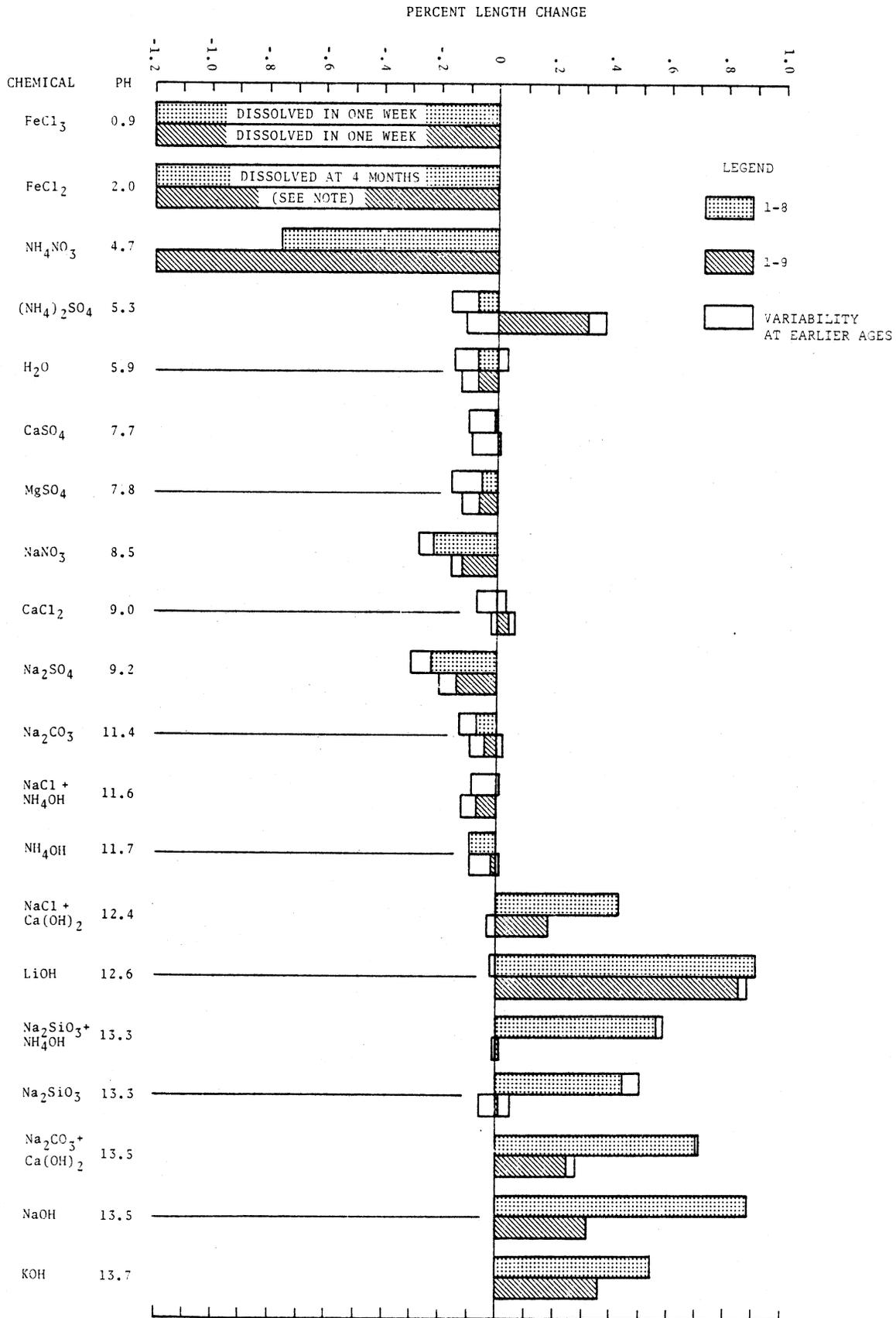


Figure 1. Graph of length changes vs. pH of chemical solution. Note: -4.321 at 7 months then completely dissolved.

TABLE 1
LISTING OF CHEMICALS USED IN ORDER OF pH, PRISMS AVAILABLE, LENGTH
CHANGES AND APPEARANCE OF PRISMS

Chemical	pH	Rock Source	Length Change at six weeks	Length Change at 13 months	Appearance
KOH	13.7	1-8	+0.194	+0.543	prism missing
		1-9	+0.185	+0.356	prism missing
NaOH	13.5	1-8	+0.418	+0.881	prism missing
		1-9	+0.132	+0.316	thin white coating
Na ₂ CO ₃ + Ca(OH) ₂	13.5	1-8	+0.359	+0.703	thick partial coating white crystals
		1-9	+0.099	+0.247	thick partial coating white crystals
Na ₂ SiO ₃	13.3	1-8	+0.360	+0.439	(missing)
		1-9	+0.063	+0.007v	clean, brown black
Na ₂ SiO ₃ NH ₄ OH	13.3	1-8	+0.375	+0.562	clean, dark brown black
		1-9	+0.071	+0.007v	white partial crust
LiOH	12.6	1-8	0	+0.910	partial coating of white crystals
		1-9	+0.042	+0.846	partial coating of white crystals
NaCl+ Ca(OH) ₂	12.4	1-8	+0.031	+0.432	thick white partial coating
		1-9	-0.008	+0.177	thick white partial coating
NH ₄ OH	11.7	1-8	-0.013	-0.094	thin white coating
		1-9	0	-0.015v	very thin white coating
NaCl+ NH ₄ OH	11.6	1-8	-0.006	+0.012v	thin powdery surface
		1-9	-0.022	-0.072	nearly clean brown-black
Na ₂ CO ₃	11.4	1-8	-0.008	-0.068	thin white crust
		1-9	-0.015	-0.038v	thin white crust
Na ₂ SO ₄	9.2	1-8	-0.098	-0.229	clean-bleached light gray
		1-9	-0.065	-0.137	clean-bleached light gray
CaCl	9.0	1-8	0	0	clean, dark brown-black
		1-9	+0.014	+0.043	clean, dark brown-black
NaNO ₃	8.5	1-8	-0.084	-0.220	clean, medium brown
		1-9	-0.041	-0.122	clean, medium brown
MgSO ₄	7.8	1-8	-0.030	-0.053	broken, clean
		1-9	-0.021	-0.064	broken, clean
CaSO ₄	7.7	1-8	-0.014	-0.014	white crust on one side
		1-9	-0.007	-0.007v	few spots of thin white coating
H ₂ O	5.9	1-8	-0.022	-0.066	minor tiny white crystals
		1-9	-0.027	-0.067	minor tiny white crystals
(NH ₄) ₂ SO ₄	5.3	1-8	-0.0129	-0.068	heavy fibrous crust, prisms bent
		1-9	-0.112	+0.314v	and broken. 1-9 held together
				shrunk first	by crystals
NH ₄ NO ₃	4.7	1-8	-0.142	-0.756	clean, very dark brown-black
		1-9	-0.211	-1.196	clean, medium brown
FeCl ₂	2.0	1-8	-0.173	(3 mo. -0.020)	
		1-9	-1.175	dissolved away (7 mo. -4.321) dissolved away	
FeCl ₃	0.9	1-8			
		1-9			dissolved away completely in one week

v signifies that the length change of the prism has varied around 0 during the time of test.

PROCEDURES

The prisms were removed from the bottles, briefly rinsed in distilled water, allowed to come to a surface dry condition, and placed individually in small vials to protect them from contamination. Each prism was mounted in a special sample holder (Figure 2) and the incrustations and the prism surfaces were used to generate X-ray diffraction patterns. A Phillips XRG 2500 with vertical goniometer, focusing monochrometer, scintillation detector and strip chart recorder was used. The various mineral and chemical species present were identified and the relative intensities of the main peaks of calcite and dolomite were used to calculate the dolomite to total carbonate ratio for the surface of each prism. In the few cases where there was a visible change in the color or texture in the rock surface diffractograms were generated from each different area and the intensity ratios averaged.

Each prism was cut in half lengthwise. By use of the same procedures, the mineral composition and the dolomite to total carbonate ratio were obtained for the center of each prism.

A longitudinal half of each prism was used to fabricate thin sections (15 - 20 μm thick) for examination with a petrographic microscope. These sections were examined at magnification up to 500x to determine the presence of reaction products and the degree of alteration of the prism components.

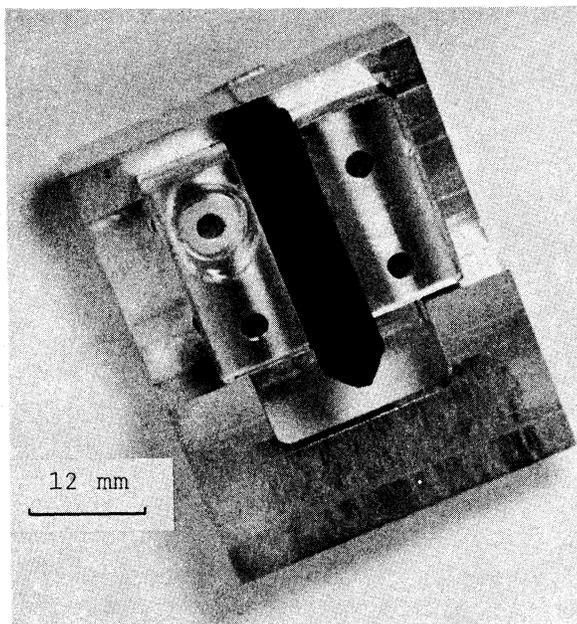


Figure 2. Prism holder used in the sample chamber of the Phillips vertical goniometer to obtain diffractograms of prism surfaces. Shown mounted is a thin slice of a prism. Note the glass surfaces adjacent to the prism to prevent any interfering reflections from the metal.

RESULTS

Petrographic Thin Sections

The results of the examination of the thin sections are summarized in Table 2.

TABLE 2

MICROSCOPIC OBSERVATION OF THIN SECTIONS OF THE PRISMS WITH THE PETROGRAPHIC MICROSCOPE

Chemical	Rock Source	Dedolomitization Detectable?	Center of Prism	Edge of Prism
NaOH	1-8	abundant	dolomite altered	dolomite gone; edges fuzzy
	1-9	abundant	dolomite altered	dolomite gone; edges fuzzy
Na ₂ CO ₃ + Ca(OH) ₂	1-8		all altered; dol. gone even from center	dolomite gone
	1-9		dol. altered in center	dolomite gone; edge firm
Na ₂ SiO ₃	1-8	missing		
	1-9	visible	dol. slightly altered	more altered at edge
Na ₂ SiO ₃ + NH ₄ OH	1-8	?	dol. not altered, clear	cal. going at edge
	1-9	visible	dol. slightly altered; mostly sharp and clear	edge weak; mostly clay remaining
LiOH	1-8	visible	whole section altered; cloudy and messy	dolomite gone; edges weak
	1-9	visible	center unaltered	dolomite altered; edge weak
NaCl+ Ca(OH) ₂	1-8	visible	dol. slightly altered	dolomite altered; edge firm
	1-9	abundant	dol. gone in center	dolomite going; edge firm
NH ₄ OH	1-8	visible	dol. not altered; clear	dol. altered on edge
	1-9	visible	dol. not altered; clear	dol. altered on edge
NaCl+ NH ₄ OH	1-8	visible	dol. slightly altered; mostly sharp and clear	edge firm
	1-9	no	no alteration; clear	no alteration
Na ₂ CO ₃	1-8	no	dol. not altered, clear	edge porous, general solution; dolomite not gone
	1-9	visible	dol. not altered, clear	dol. altered at edge
Na ₂ SO ₄	1-8	no		no alteration
	1-9	no	clear	edge a little weak; general solu.
CaCl	1-8	no	center clear	edge porous; general solution
	1-9	no	center clear	edge firm
NaNO ₃	1-8	?	minor alteration	dol. altered at edge
	1-9	no	clear	edge weak; general solution
MgSO ₄	1-8	no	clear	calcite going on edge
	1-9	no	clear	edge firm
CaSO ₄	1-8	no		no alteration
	1-9	no		no alteration
H ₂ O	1-8	no	clear	edge a little weak; general solu.
	1-9	no	clear	edge fuzzy; general solution
(NH ₄) ₂ SO ₄	1-8	no		(no section, prism, broken up and bent)
	1-9	no	Gen. disorder throughout prism; shrunk first; calcite missing	
NH ₄ NO ₃	1-8	no	clear	calcite dissolving on edge
	1-9	no	clear	calcite dissolving on edge

Examination of the thin sections did not reveal any reaction products other than calcite semi-pseudomorphic after dolomite. The hydrotalcite and brucite, which were later shown to be present in the prisms treated with NaOH and $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2$, were not detectable. It is assumed that they are fine-grained and intermingled with the clay minerals.

Both of these aggregate rocks had classical reactive texture before testing in the solutions, Figure 3. It was possible to determine the occurrence of the dedolomitization reaction by the degree of perfection of the dolomite morphology. The results of this determination are shown in Table 2 and pictures of typical areas are shown in Figures 4, 5, and 6. All the obvious cases of dedolomitization occurred in prisms tested in a pH of 12 or higher.

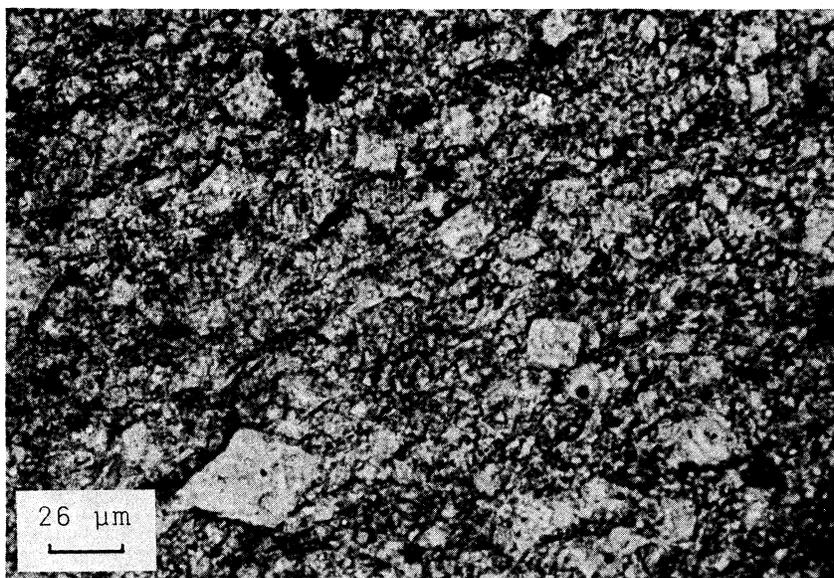


Figure 3. Photomicrograph of the unaltered interior of a prism of 1-8 aggregate soaked in distilled water. The classical reactive texture is apparent. There are small rhombs of dolomite in a calcite-clay micrite textured matrix.

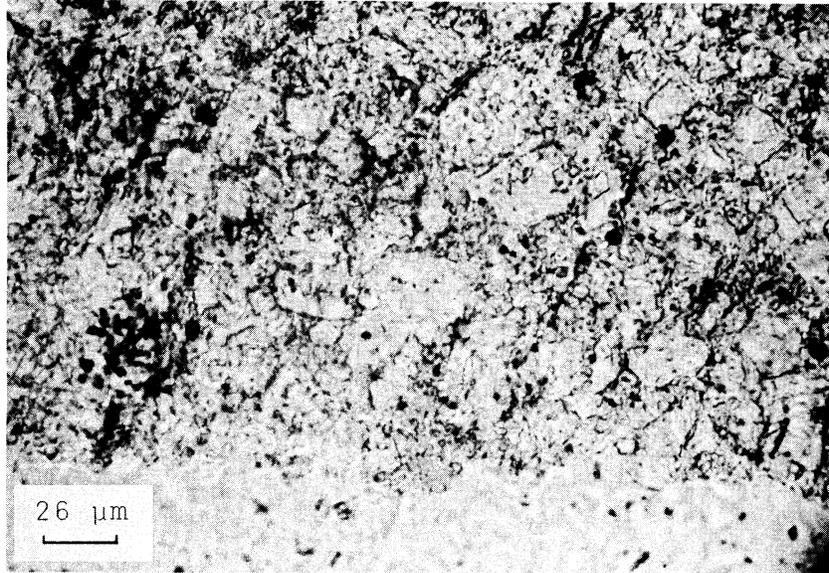


Figure 4. Photomicrograph of the edge of a prism of 1-8 aggregate soaked in a solution of $\text{NaCl} + \text{NH}_4\text{OH}$. The dolomite rhombs have lost their characteristic shape due to reaction with the solution and most are now calcite.

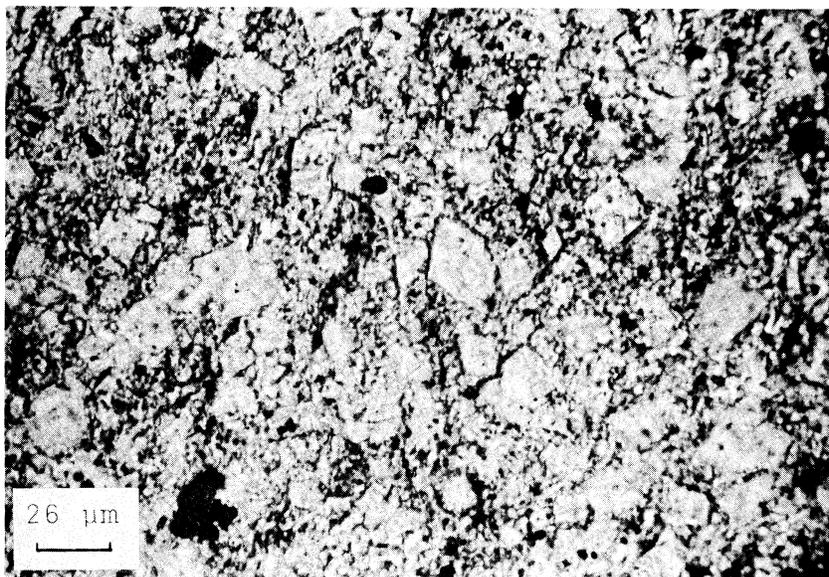


Figure 5. Photomicrograph of the interior of the prism in Figure 4. The rhombs of dolomite retain their original shape.

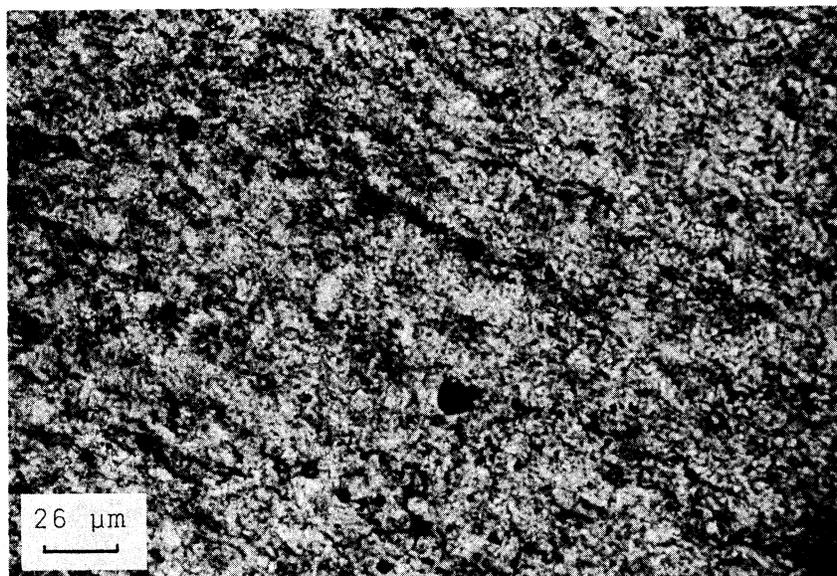


Figure 6. Photomicrograph of the interior of a prism of 1-8 aggregate soaked in a solution of $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2$. The dolomite rhombs have been altered to a fine-grained mixture of calcite and other reaction products.

X-ray Diffraction

The dolomite to total carbonate ratio found on the outside of these prisms was compared to the dolomite to total carbonate ratio found on the inside. Because the reaction had in some cases affected the inside as well as the outside, the correlation was scanty. The outside ratio was then compared to the average ratio obtained from four samples each of 1-8 and 1-9 which happened to be available. Correlations with expansions and pH were poor. The data seemed to suggest that the fresh rocks were higher in dolomite than the tested rocks had originally been. No companion samples to the prisms had been reserved from the original specimens from which the prisms were cut. The available rock having a composition most like the original composition of the exterior of the prisms is obviously the interior of those prisms which have not been affected by chemical reaction all the way to the center. The thin section evidence was used to eliminate those interior ratios which could be thought to have been altered by chemical action. For each rock type a mean of the interior ratios was calculated. This mean ratio was used as a standard to determine the ratio of the amount of dolomite altered on the outside of the prisms. These data are recorded in Table 3 and shown graphically in Figure 7. It can be seen that the

correlation within a chemical species and between rock types is quite good. Only the specimens soaked in Na_2CO_3 solution have no apparent relationship to each other. The specimens treated with NaOH solution vary greatly as to the exterior amount of dolomite changed but they both show a loss of dolomite. It can be noted that the pH has a less consistent effect on the change in the dolomite to total carbonate ratio (as shown by X-ray diffraction) than it has on the amount of expansion of these prisms. (Compare Figure 7 with Figure 1.)

TABLE 3

SUMMARY OF MINERALS DETECTED BY XRAY DIFFRACTION

Chemical	Rock Source	Minerals Detected in Prisms Other Than Original Rock Minerals*	Minerals in Exterior Powder Besides Crystallized Solution	Significant Dedolomitization Detected by Direct Comparison of Intensities	Disorder
NaOH	1-8	hydrotalcite group; brucite	calcite	*	Exteriors of Prisms show less order than interiors (lower intensities)
	1-9	hydrotalcite group	calcite & dol.	*	
$\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2$	1-8	hydrotalcite	gayluisite; gypsum calcite		
	1-9	brucite	gayluisite calcite		
Na_2SiO_3	1-8				
	1-9				
$\text{Na}_2\text{SiO}_3 + \text{NH}_4\text{OH}$	1-8				
	1-9		calcite		
LiOH	1-8		LiCO_3		
	1-9		LiCO_3		
NaCl+ $\text{Ca}(\text{HO})_2$	1-8		calcite	*	
	1-9		calcite	*	
NH_4OH	1-8				
	1-9				
NaCl+ NH_4OH	1-8				
	1-9				
Na_2CO_3	1-8				
	1-9				
Na_2SO_4	1-8				
	1-9				
CaCl	1-8				
	1-9				
NaNO_3	1-8				
	1-9				
MgSO_4	1-8		minor gypsum		
	1-9				
CaSO_4	1-8		gypsum		
	1-9				
H_2O	1-8		calcite		
	1-9				
$(\text{NH}_4)_2\text{SO}_4$	1-8		gypsum calcite		
	1-9		gypsum		
NH_4NO_3	1-8				
	1-9		dolomite		

*The natural rock minerals are assumed to be dolomite, calcite, quartz, illite and gypsum.

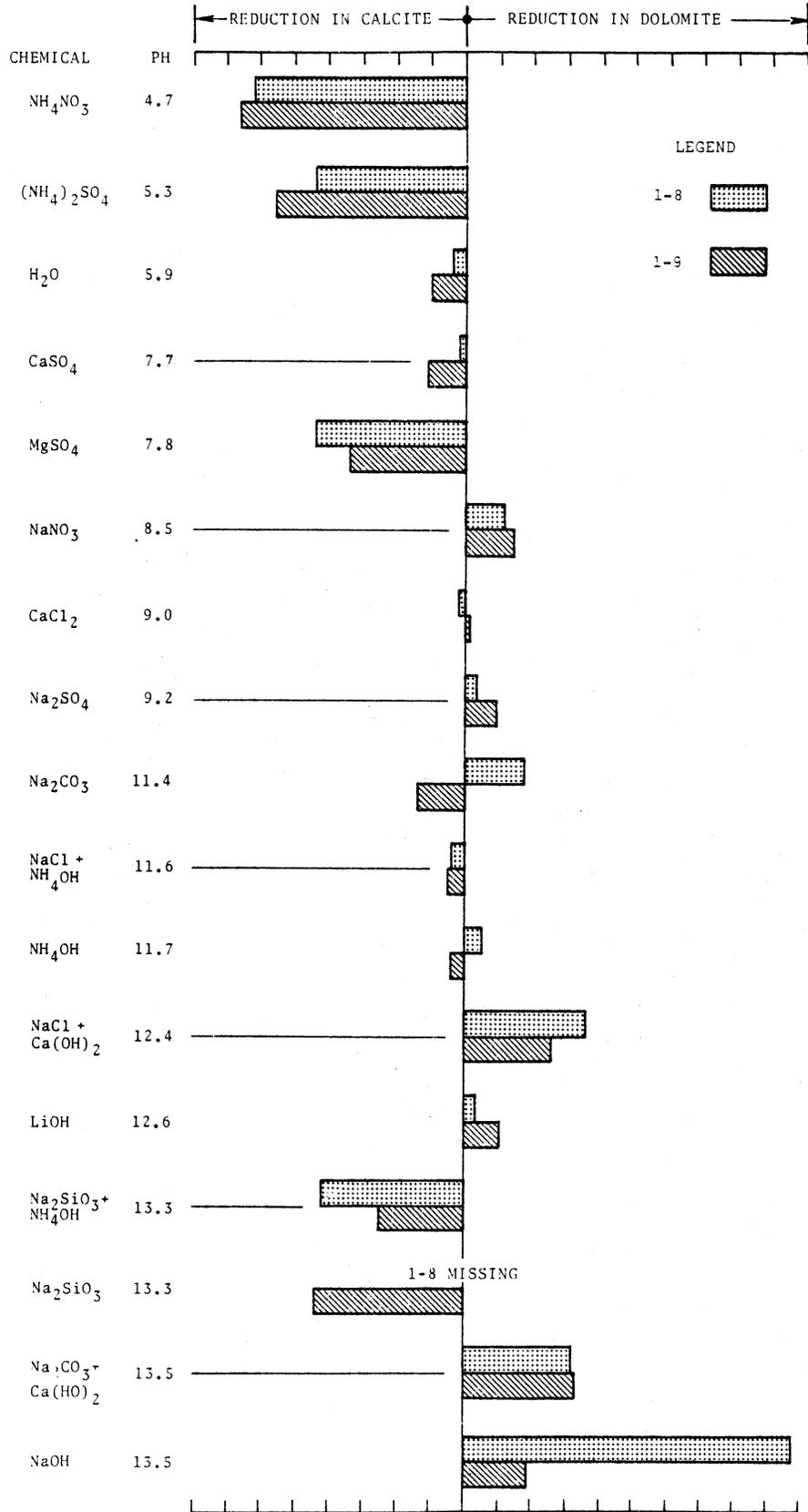


Figure 7. Graph of change in dolomite to total carbonate ratio as shown by X-ray diffraction vs. chemicals by pH.

DISCUSSION

Table 1 lists the chemicals in order of decending pH because, as was reported by Newlon and Clemeña, the long time length changes show a correlation with the pH of the solution.

From Table 1 and Figures 1 and 7, it can be seen that for any one species of chemical, aggregate 1-8 usually reacts more than does aggregate 1-9. All the chemical solutions having a pH of 13.0 or over caused an expansive reaction in aggregate 1-8 and all chemical solutions of 13.6 or over caused an expansive reaction in aggregate 1-9.

The exterior appearance of the reacted prisms appears to be mainly affected by the chemical species and only slightly affected by the difference in rock type.

Figure 7 shows removal or alteration of dolomite as positive values and removal or alteration of calcite as negative values. Thus the bars with negative values in the acid region below pH 6.3 can be interpreted as having been caused by the removal of calcite by solution so that the rock has, relative to the total carbonate content, become richer in dolomite. The chemical solutions between 6.3 and 12.1 have not caused great changes in the dolomite to total carbonate ratios on the prism surfaces. At pH 13.0 (the two Na_2SiO_3 solutions) either the dolomite has been augmented or the calcite has been removed or has become disordered. The lowered X-ray reflection intensities seen from the outside of the prism argue in favor of disorder occurring in the calcite. At and above 13.6 pH the X-ray patterns show definite reduction in the amount or degree of order in the dolomite.

Chemical Interpretations

The samples examined were composed of three major phases: (1) calcite, (2) dolomite, and (3) insoluble residue (clay). The changes in the samples after soaking in the various solutions resulted from an interaction of the solutions with one or more phases of the samples. These interactions resulted in physical changes in the samples, measured as shrinkage or expansion. Expansion results from a reaction of the solution with one or more phases, or absorption of the solution. Shrinkage results from the desorption of water from the sample or dissolution of one or more of the phases.

A major problem in analyzing the data from a chemical viewpoint is that the interactions within the sample might be complete in different modes within the phases. That is, the dolomite might expand through reactions such as proposed by Hadley, while at the same time the calcite might dissolve.

In support of this viewpoint are the samples soaked in Na_2SiO_3 solutions. These samples expanded as measured. Physical and thin section evidence revealed slight alteration of the dolomite, while at the same time the dolomite to total carbonate ratios as measured by X-ray diffraction revealed a reduction in calcite.

The higher pH's (above 12.0) showed that expansion and dedolomitization occurred more rapidly than a reduction in calcite, and, in general, the reverse was true for pH's less than 12.0.

Because of the limited number of parameters measured, it is impossible to be more definitive. Measurement of weight changes would have been of much help—but no data were taken. If another such study is made, it would be wise to consider running multiple samples, as well as increasing the number of parameters measured.

ACKNOWLEDGEMENTS

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