THE HYDRATED CALCIUM SILICATES.

I. THE SYSTEM $CaO\text{-}SiO_2\text{-}H_2O$. II. HILLEBRANDITE AND FOSHAGITE.

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ABSTRACT.

The first part of this paper reviews the system $CaO\text{-}SiO_2\text{-}H_2O$ and illustrates the relations of the various hydrated calcium silicates by means of a graph. The occurrence of anhydrous and hydrated compounds in the system is compared on a molar ratio basis. The physical and optical properties of the hydrated calcium silicates as described in the literature are summarized in tables, while a graph shows that the specific gravities of these compounds vary definitely with the composition of the minerals.

The second part presents the results of a detailed study of the minerals hillebrandite and foshagite. The results include X-ray powder data and determinations of the optical properties of both minerals. The specific gravity of foshagite was also determined. This study indicates that hillebrandite and foshagite have the same crystal structure and that differences in chemical composition and variations in optical properties may be explained as due to partial alteration of foshagite by hydrolysis and carbonation.

I. The System $CaO\text{-}SiO_2\text{-}H_2O$.

Introduction.

The problems encountered in the study of the hydration of Portland Cement[1,2] at ordinary temperatures and in the autoclave under steam pressure indicated that an investigation of the hydrated calcium silicates would give results of considerable theoretical and practical importance. Such a study has been made and it is the purpose of this paper to present a brief introductory review of the system $CaO\text{-}SiO_2\text{-}H_2O$, followed by the results obtained by chemical, optical and X-ray studies of some of the minerals belonging to this group.

The binary system $CaO\text{-}SiO_2$ has been carefully studied

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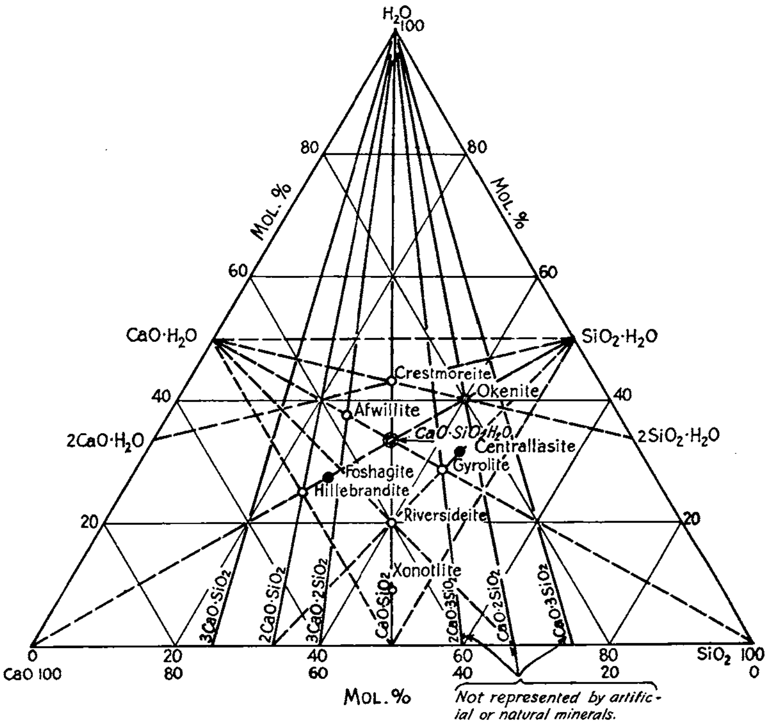
[1] Thorvaldson and Shelton, Can. J. Research. 1, 148-154, 1929.

[2] Thorvaldson and Vigfusson, Eng. J. Can. 11, 174-180, 1928.

by investigators[3] of the Geophysical Laboratory of the Carnegie Institution of Washington and forms a basis for the comparison of the hydrates. These are represented in nature by a number of rare minerals which are found occasionally in the contact zones of igneous and sedimentary rocks. The system CaO-SiO_2-H_2O is best represented by means of triangular graph, Fig. 1, which locates all the known hydrated calcium silicates according to their mol. per cent. composition as obtained from their accepted chemical formulae. The graph shows the relation of these compounds to each other and to the anhydrous calcium silicates. It should be particularly noticed that most of the hydrates occur on lines repre-



Not represented by artificial or natural minerals. See Table I

FIG. I THE COMPOSITION OF THE SYSTEM CaO-SiO_2-H_2O SHOWING MOL. PERCENT RELATIONS OF NATURALLY OCCURRING HYDRATED CALCIUM SILICATES

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[3] Day, Shepherd, Wright—This Journal, 22, 265-302, 1906.

TABLE I.

The Occurrence of Anhydrous and Hydrated Compounds in the System CaO-SiO_2-H_2O.

$CaO:SiO_2$ Molar Ratio	Anhydrous			Hydrous			
	Name	Formula	Occurrence	Name	Formula	Per Cent H_2O	Occurrence
100:0	Calcium Oxide	CaO	Artif. prep.	Calcium Hydroxide	$Ca(OH)_2$	24.3	Artif. prep.
3:1	Tricalcium Silicate	$3CaO.SiO_2$	Artif. prep.	....	....	....	None
2:1	Shannonite	$\beta 2CaO.SiO_2$	Artif. & rare minerals	Hillebrandite	$2CaO.SiO_2H_2O$	9.47	Rare mineral
	Dicalcium Silicates	$\alpha,\gamma,\beta',2CaO.SiO_2$	Artif. & rare minerals				
5:3	....	....	None	Foshagite	$5CaO.3SiO_2.3H_2O$	10.50	Rare mineral
3:2	Tricalcium-disilicate	$3CaO.2SiO_2$	Artif. prep.	Afwillite	$3CaO.2SiO_2.3H_2O$	15.78	Rare mineral
1:1	Wollastonite	$CaO.SiO_2$	Common mineral	Xonotlite	$CaO.SiO_2.O.2H_2O$	3.01	Rare mineral
	Pseudo-Wollastonite	$CaO.SiO_2$	Artif. prep.	Riversideite	$CaO.SiO_2.O.5H_2O$	7.20	Rare mineral
				Crestmoreite	$CaO.SiO_2.1.5H_2O$	18.88	Rare mineral
2:3	....	....	None	Gyrolite Reyerite	$2CaO.3SiO_2.2H_2O$	10.97	Rare minerals
4:7	....	....	None	Centrallasite	$4CaO.7SiO_2.5H_2O$	12.26	Rare mineral
1:2	....	....	None	Okenite	$CaO.2SiO_2 1.5H_2O$	16.98	Rare mineral
1:3	....	....	None	....	....	....	None
0:100	High & low Quartz.	SiO_2	Abundant Min.	Opal.	$SiO_2.nH_2O$	3.14	Common mineral
	α & β Cristobalite	SiO_2	Artif. & rare minerals	Silica Gel	$SiO_2.nH_2O$	Variable	Artif. prep.
	α, β_1, β_2, Tridymite	SiO_2	Artif. & rare minerals				

senting simple ratios of $CaO : SiO_2$ while only two minerals, foshagite and centrallasite, have the more complex ratios of 5:3 and 4:7 respectively.

It is interesting to compare the occurrence of the anhydrous and hydrous compounds of this system on the basis of their molar ratios as given in Table I.

This emphasizes the fact that the 1:1 ratio is the most stable and readily effected combination of calcium oxide and silica in either group. There are also some evident differences. Thus, there are no anhydrous compounds with a lower $CaO\text{-}SiO_2$ ratio than 1:1 while some hydrated forms of 2:3 and 1:2 ratios exist. On the other hand, we have no hydrate corresponding to the artificial $3CaO.SiO_2$, though we have three compounds in the region of 2:1 and 3:2 ratios. This may be explained by the instability of $3CaO.SiO_2$, which hydrolizes readily to give calcium hydroxide and a hydrated calcium silicate gel with a lower calcium oxide content. This indicates that a 3:1 hydrate would be extremely unstable. In the case of the 1:1 compounds we have two anhydrous forms, wollastonite and pseudo-wollastonite which are practically unaffected by water even at high temperatures (150°C.) and yet we have three stable hydrates with the same ratio. It may then be considered that the appearance of hydrates in this system is connected with the stability of the corresponding anhydrous compounds.

The physical and optical properties of the minerals recognized as practically pure hydrated calcium silicates have been described by their discoverers and various other investigators. The data so published are concisely presented in some textbooks on mineralogy[4] and are given here in the form of tables with some additional calculations by the author. See Tables II and III.

In Table III we find the molecular volumes of the compounds as calculated by two different methods; from specific gravities and molecular weights, also, by assuming fixed values for the three constituents, CaO, SiO_2 and H_2O. The values taken for these are 16.96, 22.66 and 16.26 c.c.'s respectively. Results by the two methods agree within a few per cent in most cases. Large variations occur in the case of foshagite, afwillite, xonotlite and centrallasite, which may be due to errors in the value for the specific gravity or the formula weight of each compound.

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[4] A. N. Winchell, Elements of Optical Mineralogy, 2d Ed., Part II, p. 226.

TABLE II.

Optical Properties of Hydrated Calcium Silicates

Mineral	Crystal System	Habit	Elongation	Indices of Refraction Np	Nm	Ng	Optic Angle 2V.	Optical Character
Okenite	Orth.	Fibrous	γ	1.512	1.514	1.515	Large	Negative
Centrallasite	Orth.	Fibrous	γ	1.535	....	1.549	Small	Negative
Gyrolite Reyerite	Rhomb.	Lamellar	..	1.535	....	1.545	Uniaxial	Negative
Crestmoreite	Mon.?	Fibrous	γ	1.593	1.603	1.607	?	Negative
Riversideite	?	Fibrous	γ	1.595	1.60	1.603	?	?
Xonotlite	Orth.?	Fibrous	γ	1.583	1.583	1.593	Small	Positive
Afwillite	Mon.	Prismatic	β	1.617	1.620	1.634	54.7°	Positive
Foshagite	Orth.	Fibrous	γ	1.594	1.594	1.598	v. small	Positive
Hillebrandite	Orth.	Fibr. prism	γ	1.605	1.61	1.612	70°	Negative

TABLE III.

Other Physical Properties of Hydrated Calcium Silicates.

Name	Formula	Mol. Wt.	Sp. Gr.	Mol. Vol. $\frac{\text{(Mol. Wt.)}}{\text{(Sp. Gr.)}}$	Mol. Vol. (Calc.)	Hardness	Fusibility	Chemical Behaviour
Okenite	$CaO..2SiO_2.2H_2O$	212.2	2.28	93.1	94.8	4.5-5	easy	gel. in acid
Centrallasite	$4CaO.7SiO_2.5H_2O$	734.4	2.43	302.2	307.8	3-4	diff.	Sol. in HCl.
Gyrolite Reyerite	$2CaO.3SiO_2.2H_2O$	328.4	2.43	135.1	134.4	3-4	diff.	Sol. in HCl.
Crestmoreite	$2CaO.2SiO_2.3H_2O$	286.3	2.22	129.0	128.0	3	easy	Sol. in HCl.
Riversideite	$2CaO.2SiO_2.H_2O$	250.3	2.64	94.8	95.5	3	easy	Sol. in HCl.
Xonotlite	$5CaO.5SiO_2.H_2O$	598.7	2.70	221.8	214.4	6.5	easy	Sol. in HCl.
Afwillite	$3CaO.2SiO_2.3H_2O$	342.4	2.63	130.2	145.0	4	diff.	Sol. in HCl.
Foshagite	$5CaO.3SiO_2.3H_2O$	514.6	2.36	218.0	201.6	3	diff.	Sol. in HCl.
Hillebrandite	$2CaO.SiO_2.H_2O$	190.2	2.69	70.7	72.8	5.5	diff.	Sol. in HCl.

Specific Gravity.

The variations in specific gravity and composition of the hydrated calcium silicates are represented in Fig. 2. The specific gravity is definitely dependent on the degree of hydration and varies to less extent with changes in molar ratios of CaO : SiO_2 of the compounds. Thus the density decreases with increasing percentage of water and decreasing calcium oxide content. The graph shows that foshagite has a specific gravity which is much too low for its position in the series.

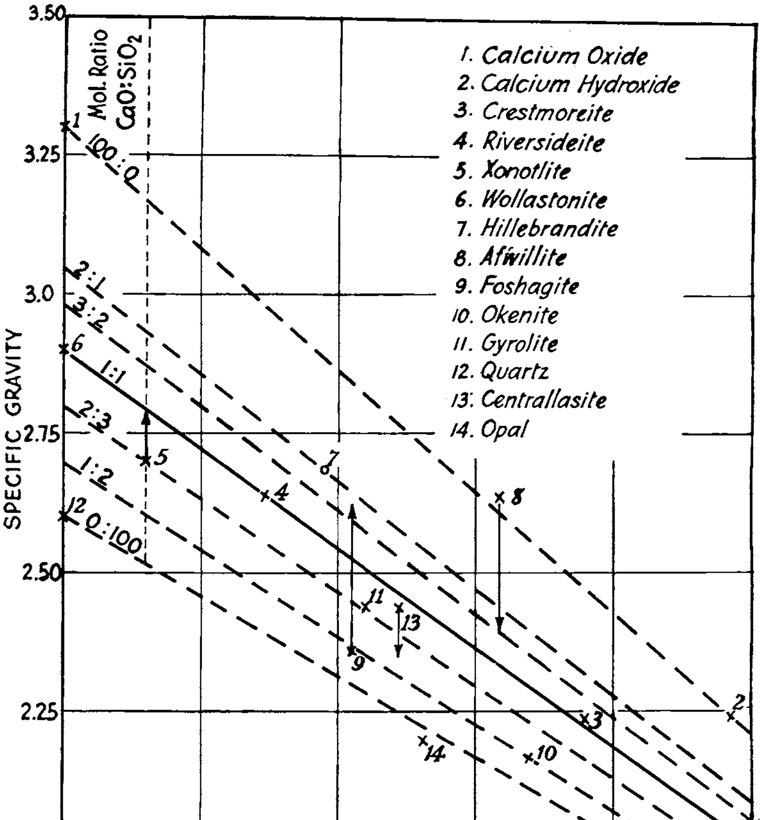

FIG. 2 VARIATIONS IN SPECIFIC GRAVITY AND COMPOSITION OF COMPOUNDS IN THE SYSTEM $CaO-SiO_2-H_2O$

The specific gravity of xonotlite is also a trifle low, while afwillite and centrallasite appear to have higher specific gravities than would be expected. It will be shown later that the specific gravity of foshagite is actually higher than the value given in the literature. The arrows in the graph indicate the theoretical positions for the above named minerals.

Summary.

The system $CaO-SiO_2-H_2O$ includes a number of rare natural minerals, whose physical and optical properties have been more or less accurately described. The hydrated minerals are compared as to composition and occurrence with the corresponding anhydrous compounds. All the hydrated calcium silicates except foshagite and centrallasite appear to have compositions involving simple ratios of $CaO:SiO_2$. The compounds having a 1:1 ratio are most numerous and may be considered the most stable. Further, there appears to be a definite relation between the specific gravity and the composition of each mineral in the system. Thus the specific gravity decreases with increasing water content and decreasing proportion of calcium oxide. Deviations from the theoretical positions are found for the minerals foshagite, centrallasite, afwillite and xonotlite. These deviations may be due in some cases to errors in determining the specific gravity or the chemical composition.

II. HILLEBRANDITE AND FOSHAGITE.

A sample of hillebrandite was obtained from Ward's Science Establishment, Rochester, N. Y. It is labelled from the Velardena mine, Durango, Mexico, which is the location of the original specimens described by F. E. Wright. The sample is a dense, pearly white material with some tint of green and is composed of a conglomeration of small fibers, flakes and irregular grains.

Samples of foshagite were obtained from Ward's and from A. Pabst of the University of California. These are identical and are from Wet Weather Quarry, Crestmore, California. Both samples are coarsely fibrous, resembling fossilized wood, and have a dull gray color. This suggests surface weathering of the samples to some extent. The coarse fibers are found to consist of parallel arrangements of very long, fine, lath-shaped crystal fibers.

X-Ray Patterns of Hillebrandite and Foshagite.

Photographs of the X-ray diffraction patterns of these minerals were made with a multiple powder spectrograph, manufactured by the General Electric Company. A Coolidge tube with water-cooled molybdenum target was the source of X-rays and a zirconia filter was used in front of the film.

TABLE IV.

Data obtained from powder photographs of hillebrandite and foshagite.

Hillebrandite		Foshagite	
Planar spacings. d_{hkl} in Å	Estimated relative intensity.	Planar spacings. d_{hkl} in Å	Estimated relative intensity.
4.9	W		
3.51	W	3.51	W
3.34	M	3.33	M
3.13	W		
2.93	SS	2.93	SS
2.79	M	2.80	W
2.68	W	2.67	W
2.46	M	2.48	W
2.38	WW	2.37	W
2.30	M	2.32	W
2.22	W	2.25	W
2.16	M	2.17	M
2.10	W	2.11	WW
2.04	M	2.05	M
1.960	M	1.965	M
1.875	W	1.872	W
1.820	S	1.822	S
1.737	S	1.742	S
1.675	WW		
1.623	WW	1.627	W
1.595	M	1.595	W
1.560	WW		
1.528	M	1.532	W
1.507	W	1.510	W
1.467	W	1.473	W
1.442	W	1.448	W
1.432	W	1.431	W
1.350	W		
1.301	W		
1.262	M	1.260	M
1.210	W	1.214	W
1.183	M	1.183	M
1.149	M	1.152	W
1.121	M	1.122	M
		1.088	WW
1.060	M	1.061	M
1.038	M	1.040	M

SS, Very strong; S, strong; M, medium; W, weak; WW, very weak.

The usual procedure of the powder method was followed and needs no description. The planar spacings of each pattern were read directly on the scale provided with the apparatus. Pure sodium chloride was used as a standard for comparison. The relative intensity of each diffraction line was estimated and described as strong, medium or weak, etc. The data obtained are presented in Table IV.

The X-ray diffraction patterns of hillebrandite and foshagite thus prove to be practically identical and indicate that the arrangement of the atoms in the two forms is essentially the same. The two patterns differ considerably in the intensity of their lines but the planar spacings agree within the limits of experimental error. The intensity of the lines in the pattern of foshagite is generally weaker than in the case of hillebrandite and some of the very weak diffraction lines are therefore missing. This fact is most likely due to the longer fibers in the foshagite which were not readily reduced by grinding, or to the presence of some absorbing material.

The differences in chemical composition, density and some optical properties of these two minerals, as reported in the literature (see Tables III, IV and V) therefore require correction or explanation. The differences in the chemical analyses (Table V) may be explained as being due to partial

TABLE V.

Chemical Analyses of Hillebrandite† and Foshagite.‡

	Hillebrandite	Foshagite	Theor. $2CaO.SiO_2.H_2O$	Theor. $5CaO.3SiO_2.3H_2O$
SiO_2	32.59	33.92	31.74	35.62
TiO_2	.02	....	....	....
Al_2O_3	.23	....	....	....
Fe_2O_3 FeO }	.15	.83	....	....
MnO	.10	....	....	....
MgO	.04	trace	....	....
CaO	57.76	53.48	58.81	53.68
Na_2O	.03	....	....	....
K_2O	.05	....	....	....
F	none	....	....	....
CO_2	none	1.83	....	....
H_2O	9.36	10.19	9.45	10.70
	100.24	100.25	100.00	100.00

† Analysis by E. T. Allen, analyst, reported by F. E. Wright.[6]
‡ Analysis reported by A. S. Eakle.[7]

alteration of one mineral, foshagite. Two factors may be considered. First, there is some hydrolysis of these minerals when they are in contact with water. Calcium hydroxide is liberated and amorphous silica left as a residue. This is readily demonstrated by shaking some of the powdered mineral in distilled water containing phenolphthalein indicator. A strong pink color is instantly developed due to the liberation of calcium hydroxide. A thin section of foshagite shows the presence of considerable amounts of amorphous alteration products which are believed to be silica gel produced by hydrolysis. This contention is supported by the fact that foshagite is readily stained by methylene blue, while hillebrandite is only slightly tinted in spots. Methylene blue is readily absorbed by colloidal silica and has been used for identifying amorphous silica in cement materials by Kaisermann.[5]

The second factor to be considered is carbonation. The analysis of foshagite shows nearly two per cent of carbon dioxide which may be due to inclusions or more likely due to the action of soluble carbonates or carbonic acid on the mineral. The fibers of foshagite, under high magnification, show small bright grains of calcite scattered on their surfaces as if the calcium carbonate had been deposited from solution.

The net result of these two processes, hydrolysis and carbonation, would be a reduction in calcium oxide and an increase in silica content of the mineral and the final composition would depend on the extent to which each had operated. Foshagite actually contains more silica and less calcium oxide than hillebrandite as this explanation requires.

Specific gravity of foshagite.

The specific gravity of foshagite was determined on the finely powdered material by displacement of pure benzene at 25° C. A specific gravity bottle of 25 c.c. capacity was used and the temperature maintained constant by means of a thermo-regulated oil-bath. Duplicate results gave an average value of 2.67 for the specific gravity of foshagite as against 2.36 reported by Eakle. The value here obtained agrees fairly well with the value of 2.69 found by Wright for hillebrandite. The slightly lower value would be expected if the mineral contains an appreciable amount of amorphous silica.

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[5] Cement & Engineering News, 23, 62, 1911.

Optical Properties of Hillebrandite and Foshagite.

The optical properties of hillebrandite and foshagite were determined by the examination of thin sections and individual grains. The Emmons double variation method was used to determine indices of refraction. A measure of the optic angles was obtained by calculation from indices of refraction, using the exact equation:

$$\text{Cos}^2\text{V}_a = \frac{\gamma^2(\beta^2 - a^2)}{\beta^2(\gamma^2 - a^2)}.$$

The results obtained are summarized in Table VI, which may be compared with formerly accepted data given in Table II.

TABLE VI.

Optical Properties of Hillebrandite and Foshagite.

	Hillebrandite	Foshagite
Microscopic Appearance.	Irregular fibrous plates, sometimes radiating; inclusions of garnet and wollastonite; small amount of amorphous material.	Long parallel fibers; considerable amorphous matter. Some calcite as very small crystals on the surface of the fibers.
Crystal System ..	Orthorhombic	Orthorhombic
Habit	Fibrous	Fibrous
Cleavage	Parallel to fibers	Parallel to fibers
Elongation	Positive	Positive
Extinction	Parallel	Parallel
Optical orientation	$Z = c$ $X = a$ and $Y = b$	$Z = c$ $X = a$ and $Y = b$
Dispersion	$\rho > V$	$\rho > V$
Optic Angle, 2V..	60° ±	60° ±
Opt. char.	Negative	Negative
Indices of Ref. N^g	1.612	1.605
N^m	1.610	1.603
N^p	1.604	1.597
Birefringence. $N^g - N^p$	0.008	0.008

The description of the optical properties of hillebrandite by F. E. Wright[6] is thus verified in practically every respect. The optical properties of foshagite are found to be somewhat different from those reported by A. S. Eakle[7] but differ from those of hillebrandite only in indices of refraction. The optical character of foshagite is found to be negative instead of positive. The values for indices of refraction are higher than those formerly accepted, but are slightly lower than the

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[6] F. E. Wright, this Journal, 26, 551, 1908.

[7] A. S. Eakle, Am. Mineral, 10, 97, 1925.

indices of hillebrandite. It is found that coarse fibers of foshagite have much lower indices than the fine fibers separated from it. This is particularly evident when amorphous matter is obviously present. It is therefore possible that even the finest fibers have a thin coating of amorphous silica which affects the indices as measured by the immersion method.

Conclusion.

This study of the minerals hillebrandite and foshagite may be briefly summarized as follows:

1. X-ray data show that hillebrandite and foshagite have the same crystal structure.
2. Differences in the chemical composition of the two minerals are most likely due to partial hydrolysis and carbonation of foshagite.
3. The specific gravity of foshagite is found to be 2.67, a value only slightly less than that of hillebrandite.
4. The optical properties of the minerals are very similar.
5. Differences in indices of refraction are probably due to the presence of a thin film of amorphous silica on the fibers of foshagite.

We thus come to the conclusion that hillebrandite and foshagite are really the same hydrated calcium silicate $2CaO.SiO_2.$-H_2O; but differ in crystal habit and degree of alteration by the processes of hydrolysis and carbonation.

A continuation of this study is in progress and results on the other known hydrated calcium silicates, including artificial preparations, are to be published in the near future.

Acknowledgments.

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