

In experiment 41 more than 50 percent of the anhydrous tricalcium disilicate, treated with water at 150° C for 6 weeks, remained unaltered. The alteration product consisted of irregular masses of low-birefringent material of refractive index 1.57, and was not identified. This material kept an additional 10 days at 250° C (experiment 44) was largely altered to low-birefringent aggregates of mean refractive index, 1.62+. The X-ray pattern was different from that of afwillite and could not be identified.

Treatment of anhydrous tricalcium disilicate with water at 500° C, 380 atmospheres, for 2 weeks (experiment 49) resulted in 90-percent conversion to a new phase. Inasmuch as the tricalcium disilicate contained a few percent of impurities (mostly dicalcium silicate) there were also present some alteration products of the impurities, including some dicalcium silicate hydrates, the hydrothermal formation of which will be described subsequently. The new phase consisted of small needle- and lath-shaped crystals of parallel extinction and positive elongation. The indices of refraction are: $\alpha=1.608 \pm 0.003$, $\gamma=1.615 \pm 0.003$. A photomicrograph of these crystals is shown in figure 8.

Determinations of ignition loss showed the new compound to be anhydrous. Its X-ray pattern proved to be different from that of ordinary tricalcium disilicate or any of the other anhydrous calcium silicates. Ignition for a few minutes over a Méker burner converted it back to the usual form of tricalcium disilicate.

The evidence indicated that the new phase was a low-temperature form of tricalcium disilicate. This was confirmed by experiments using the quenching method. A sample held overnight at 1,020° C gave an unchanged X-ray pattern, while a sample held at 1,027° C overnight gave the pattern of ordinary tricalcium disilicate. The inversion of the low-temperature form of tricalcium disilicate to the high-temperature form is therefore placed at $1,024^{\circ}\text{C} \pm 5^{\circ}\text{C}$.

Attempts to prepare the mineral afwillite were unsuccessful. Amorphous hydrates having the CaO/SiO_2 molar ratio of this compound when heated at temperatures of 150° and 200° C in the presence of water crystallized largely to $\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$, and at temperatures ranging from 250° to 400° C crystallized largely to xonotlite. The secondary phases could not be distinguished petrographically or by the X-ray patterns. Raising the CaO/SiO_2 molar ratio has the effect of making both $\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ and xonotlite stable at higher temperatures than was the case with the preparations of pure hydrated monocalcium silicate.

(f) MOLAR RATIO CaO/SiO_2 , 5:3

The compositions treated in the experiments reported in table 7 corresponded in lime-silica ratio to the mineral foshagite, $5\text{CaO}\cdot 3\text{SiO}_2\cdot 3\text{H}_2\text{O}$.

TABLE 7.—Results of experiments on $5\text{CaO}:3\text{SiO}_2$ compositions

Experiment number	Starting material	Temper- ature	Pressure	Time	Product
		$^{\circ}\text{C}$		Days	
50.....	1.67 $\text{CaO}:\text{SiO}_2$ glass ¹	200	15	73	?
51.....	do.....	300	85	53	Foshagite+glass.
52.....	do.....	350	163	17	Foshagite+glass.

¹ Contained 7 percent of B_2O_3 .

The product of experiment 50 had the same X-ray pattern as that of the product obtained by treating anhydrous dicalcium silicate and dicalcium silicate glass with water at relatively low temperatures, and will be discussed in the next section.

The product of experiments 51 and 52 was a low-birefringent material without definite crystalline form and of mean index of refraction 1.595, which checks well with the mean index of foshagite. The X-ray patterns showed complete correspondence with the X-ray pattern of foshagite obtained from the United States National Museum. Conversion of the glass to the hydrate was not complete even in experiment 51, as the product gave an ignition loss of only 5.7 percent, compared with a theoretical loss for foshagite of 10.5 percent.

A sample of amorphous hydrate of CaO/SiO_2 molar ratio 1.68 steamed at 300°C out of contact with water gave a product having the X-ray pattern of $\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$. The manner of combination of the excess lime could not be determined.

(g) MOLAR RATIO CaO/SiO_2 , 2:1

Results of experiments on compositions having a dicalcium silicate molar ratio, to which the mineral hillebrandite, $2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$, corresponds, are listed in table 8.

TABLE 8.—Results of experiments on $2\text{CaO}:1\text{SiO}_2$ compositions

Experiment number	Starting material	Temperature	Pressure	Time	Product
		$^\circ\text{C}$	atm		
53	$\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$	25	1	10 years	?
54	do	100	1	9 days	$10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O} + \beta\text{-}2\text{CaO}\cdot\text{SiO}_2$
55	$\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$	150	5	4 days	$10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O} + \gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$
56	$\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$	150	5	1 day	Scarce $10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O} + \beta\text{-}2\text{CaO}\cdot\text{SiO}_2$
57	do	150	5	7 days	Pure $10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$
58	$2\text{CaO}:\text{SiO}_2$ gel	150	5	10 days	95% of $10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$
59	$2\text{CaO}:\text{SiO}_2$ glass (12% of B_2O_3)	150	5	23 days	Same as preparation 53.
60	90% of $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$ + 10% of natural hillebrandite.	150	5	14 days	$10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$ + natural hillebrandite.
61	Preparation 53	175	9	41 days	Same product as preparation 53.
62	$\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$	200	15	3 days	$10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$
63	$2\text{CaO}:\text{SiO}_2$ gel	225	25	44 days	$2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$
64	$3\text{CaO}:2\text{SiO}_2$ aq + CaO	225	25	47 days	$\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O} + ?$
65	$\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$	250	39	15 days	$2\text{CaO}\cdot\text{SiO}_2$ aq.
66	$10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$	250	39	14 days	$10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$
67	90% of $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$ + 10% of natural hillebrandite.	250	39	14 days	Natural hillebrandite + $2\text{CaO}\cdot\text{SiO}_2$ aq.
68	$3\text{CaO}:2\text{SiO}_2$ aq + CaO	300	85	7 days	$\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O} + ?$
69	do	350	163	8 days	$\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O} + 3\text{CaO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}$
70	$10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$	450	400	7 days	$2\text{CaO}\cdot\text{SiO}_2\cdot 2/3\text{H}_2\text{O}$

Five g of β -dicalcium silicate treated with 500 ml of water for 10 years at room temperature (experiment 53) and shaken at intervals gave a product having a distinctive X-ray pattern and possessing a composition corresponding to the ratios $1.8\text{CaO}:1.0\text{SiO}_2:2.1\text{H}_2\text{O}$. It contained about 5 percent of calcite with the bulk of the material consisting of weakly birefringent masses without definite crystalline form. In order to effect further crystallization this material was

heated in the presence of water for 6 weeks at a temperature of 175° C (experiment 61). It was then completely crystallized to very fine needles of low birefringence and mean index of refraction 1.60. A chemical analysis gave the composition: 52.94 percent of CaO, 0.78 percent of R₂O₃, 36.50 percent of SiO₂, 9.69 percent of H₂O, which corresponds to the molar ratios: 1.55CaO:1.00SiO₂:0.88H₂O. Allowing for the calcite which the sample contained, this analysis agrees fairly well with the formula 3CaO.2SiO₂.1.5H₂O. The pattern is not like that of awillite. The same X-ray pattern was given by dicalcium silicate glass (containing 12 percent of B₂O₃) treated with water at 150° C for 3 weeks (experiment 59) and also by 5CaO.3SiO₂ glass (containing 7 percent of B₂O₃) at 200° C for 10 weeks (experiment 50, table 7).

Treating dicalcium silicate with water between 100° and 200° C usually produces an orthorhombic hydrate of dicalcium silicate. This compound is identical with crystals found by Thorvaldson and Shelton [17] in steam-cured portland cement and prepared in a pure state by Vigfusson, Bates, and Thorvaldson [18]. Reference to the preparation of the same compound from mixtures of lime, silica, and water and from tricalcium silicate and water has also been made by Flint and Wells [6]. The crystals are extremely thin (rarely more than 3 microns in thickness), lath-like plates often occurring as simple rectangular parallelepipeds but not infrequently with domatic faces beveling the prismatic forms. The measured indices of refraction agree with those fixed by previous investigators: $\alpha=1.614\pm 0.002$, $\beta=1.620\pm 0.002$, $\gamma=1.633\pm 0.002$. The crystals are biaxial positive. There is a perfect cleavage normal to the elongation. A photomicrograph is shown in figure 9.

Analysis of a typical preparation gave the composition: 56.64 percent of CaO, 0.46 percent of R₂O₃, 31.14 percent of SiO₂, and 11.34 percent of H₂O, corresponding to the ratios: 1.96CaO:1.00SiO₂:1.19H₂O. Prolonged heating in an oven maintained at a temperature of 110° C reduced the water content to 10.90 percent, which corresponds to a H₂O/SiO₂ molar ratio of 1.17. Analysis of several other preparations also gave water contents corresponding closely to 1.2H₂O:1.0SiO₂. The average of three analyses of this compound presented by Vigfusson, Bates, and Thorvaldson [18] likewise gave a H₂O/SiO₂ molar ratio of 1.24. It, therefore, appears probable that the water in excess of 1 mole is constitutional, and accordingly, the formula 10CaO.5SiO₂.6H₂O is suggested for the compound.

As shown in table 8, 10CaO.5SiO₂.6H₂O resulted from treatment with water of β - and γ -dicalcium silicates and 2CaO:1SiO₂ mixtures of calcium oxide and silica gel. At 100° C (experiment 54), 9 days' boiling of 1 g of β -dicalcium silicate with 25 ml of water under a reflux gave about 30-percent conversion to 10CaO.5SiO₂.6H₂O. Well-formed crystals of 10CaO.5SiO₂.6H₂O were also obtained by treatment of portland cement clinkers with water at 100° and 175° C. A photomicrograph of the product obtained at 175° C is given in figure 10.

Attempts to prepare hillebrandite by treating mixtures of natural hillebrandite and dicalcium silicate with water at 150° and 200° C (experiments 60 and 67) were unsuccessful. The results obtained by Kohler [16], who reported having prepared hillebrandite by heating a mixture of β -dicalcium silicate and water at temperatures ranging from 200° to 290° C, could not be duplicated. The synthesis of hille-

brandite from mixtures of CaO and amorphous SiO₂ in the presence of CaCl₂ heated with water at 470° C has been claimed by Schlaepfer and Niggli [10].

Treatment of 10CaO.5SiO₂.6H₂O at 250° C for 2 weeks (experiment 66) produced no change; treatment at 450° C, 400 atmospheres, for 1 week gave a product of unchanged crystal form but having the indices of refraction: $\alpha=1.642$, $\gamma=1.672$, which are about 0.03 higher than the corresponding indices of 10CaO.5SiO₂.6H₂O. This material gave a distinctive X-ray pattern and its composition corresponded to the formula, 6CaO.3SiO₂.2H₂O.

In experiment 65, β -dicalcium silicate heated in a bomb with water at 250° C crystallized to a granular product having a mean index of refraction of 1.64. The X-ray pattern was similar in spacing and intensity of lines to that of a finely crystalline monohydrate of dicalcium silicate obtained by Keevil and Thorvaldson [19]. Treatment of a 2CaO:1SiO₂ mixture of CaO and silica gel at 225° C (experiment 63) gave complete crystallization to the other monohydrated dicalcium silicate described by Thorvaldson and coworkers [18, 19]. This occurs in very small needles of low birefringence and mean index 1.60. Analysis gave a composition corresponding to the ratios 2.0CaO:1.0SiO₂:1.1H₂O.

In experiments 64, 68, and 69 amorphous hydrated calcium silicate of CaO/SiO₂ molar ratio 3:2 was mixed with sufficient CaO to give a ratio of 2:1 and in the presence of water heated at temperatures of 225°, 300°, and 350° C. The principal product in all three cases was CaO.SiO₂.H₂O. The secondary product was not identified except in experiment 69, where the optical properties and X-ray pattern showed it to be a hydrate of tricalcium silicate.

(b) MOLAR RATIO CaO/SiO₂, 3:1

The results of these experiments are shown in table 9.

In experiment 71, 1 g of tricalcium silicate treated with 500 ml of water for 9 years at room temperature was completely converted to a hydrated material of composition 1.3CaO:1.0SiO₂:1.7H₂O. Petrographic examination showed less than 5 percent of calcite with the bulk of the material appearing as rounded grains of low birefringence having refractive indices ranging from 1.52 to 1.53. The X-ray pattern of this material was different from that of calcite or any of the other hydrous or anhydrous calcium silicates thus far investigated.

TABLE 9.—Results of experiments on 3CaO:SiO₂ compositions

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	atm		
71	3CaO.SiO ₂	25	1	9 years	?
72	do	100	1	14 days	10CaO.5SiO ₂ .6H ₂ O+Ca(OH) ₂ .
73	do	150	5	5 days	Do.
74	do	200	15	35 days	3CaO.SiO ₂ .2H ₂ O+10CaO.5SiO ₂ .6H ₂ O+Ca(OH) ₂ .
75	do	250	39	12 days	3CaO.SiO ₂ .2H ₂ O.
76	β -2CaO.SiO ₂ +CaO	250	39	10 days	2CaO.SiO ₂ hydrate+Ca(OH) ₂ .
77	3CaO:2SiO ₂ :aq+3CaO	275	59	16 days	3CaO.SiO ₂ .2H ₂ O.
78	3CaO.SiO ₂	350	163	8 days	Do.
79	do	450	397	6 days	Do.

Tricalcium silicate treated with water at 100° C under a reflux condenser (experiment 72) and in the bomb at 150° C (experiment 73)

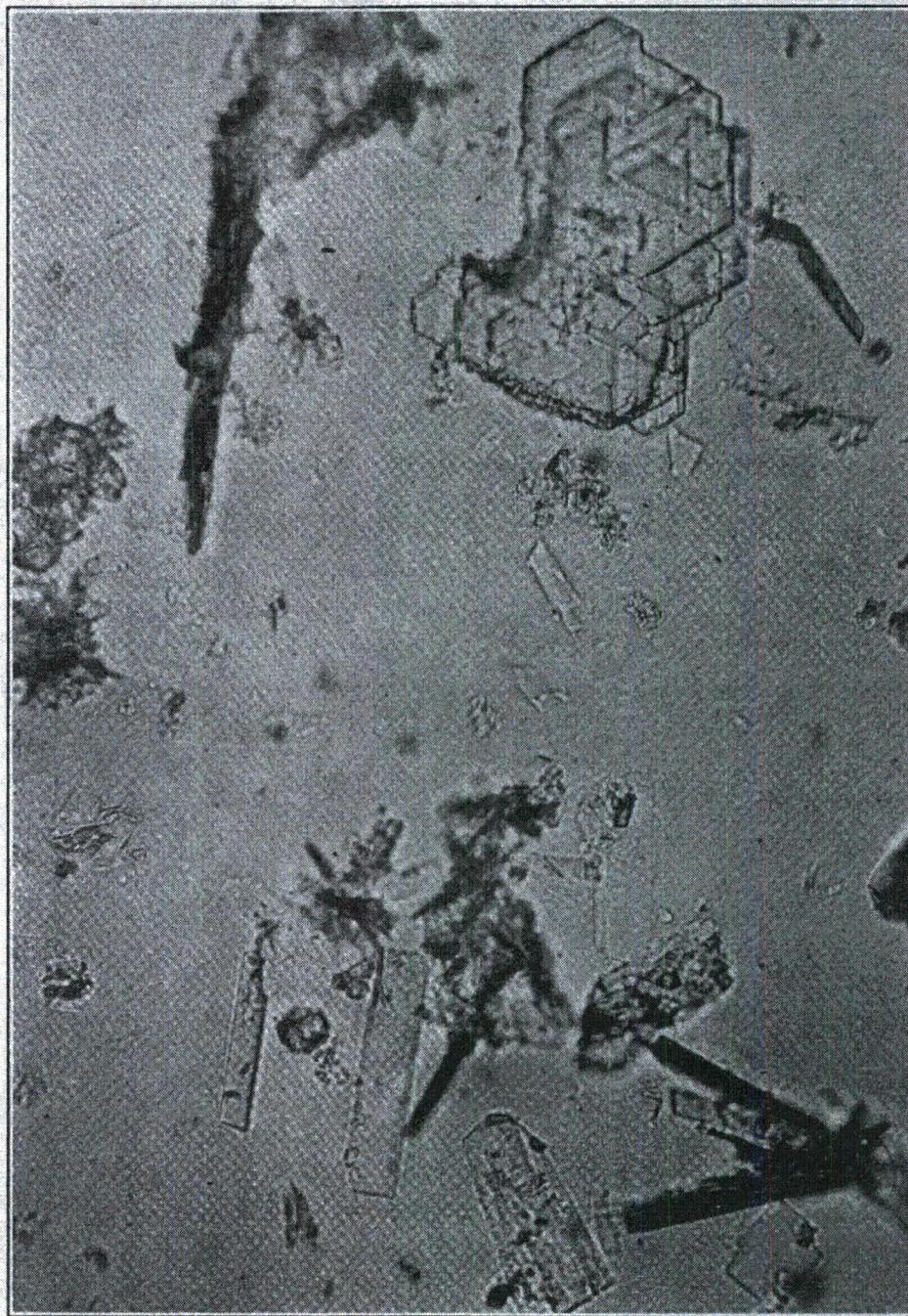


FIGURE 10.—Lath-like orthorhombic plates of synthetic $10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$ and hexagonal plates of $\text{Ca}(\text{OH})_2$ obtained by treatment of portland cement clinker with water at 175°C .

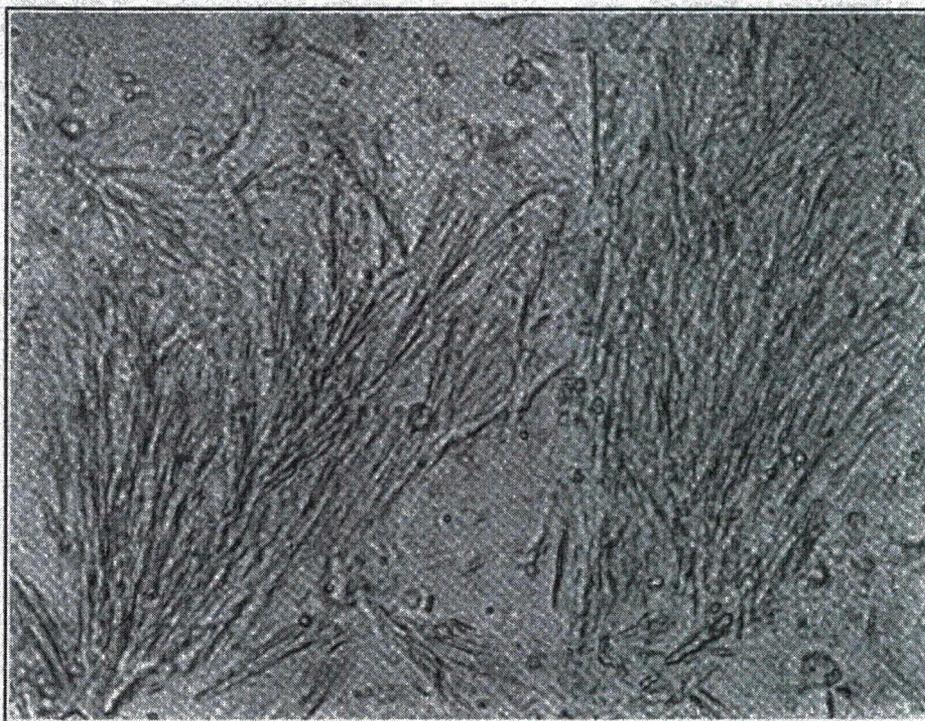


FIGURE 11.—*Synthetic* $3\text{CaO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}$.
Magnification $\times 900$.

was converted to $10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$ and calcium hydroxide. At 250°C (experiment 75) direct hydration occurred without liberation of calcium hydroxide. The product consisted of broad fibrous crystals of positive elongation and parallel extinction. The indices of refraction were: $\alpha=1.590 \pm 0.003$, $\gamma=1.602 \pm 0.003$. Analysis of the preparation from experiment 75 gave the composition: 65.42 percent of CaO, 23.45 percent of SiO_2 , 11.53 percent of H_2O , corresponding to the ratios: $2.98\text{CaO}:1.00\text{SiO}_2:1.63\text{H}_2\text{O}$. At 200°C (experiment 74) the product was primarily this compound with smaller amounts of $10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ also present.

For experiment 77 the starting material was a mixture of amorphous hydrate of CaO/SiO_2 molar ratio 3:2 mixed with sufficient CaO to give a ratio of 3:1. After 16 days in the bomb at 275°C this preparation crystallized completely to large broom-shaped clusters of fibrous needles having the composition: 63.07 percent of CaO, 0.50 percent of R_2O_3 , 22.38 percent of SiO_2 , 13.56 percent of H_2O , corresponding to the ratios: $3.02\text{CaO}:1.00\text{SiO}_2:2.02\text{H}_2\text{O}$. A photomicrograph of this material is shown in figure 11. The X-ray pattern and optical properties were the same as those of the product from direct hydration of anhydrous tricalcium silicate. This preparation and that of experiment 75 gave negative tests for free lime by alcohol-glycerol extraction and by White's method.

This compound is identical with the product obtained by Keevil and Thorvaldson [19] by steaming tricalcium silicate between 110° and 375°C . By their procedure, however, only very finely crystalline material resulted.

Dehydration experiments proved the hydrated tricalcium silicate to be a very stable compound. A preparation heated in an oven for 16 hours at 215°C gave a loss in weight of only 0.2 percent. At 500°C for 16 hours the loss was 2.6 percent and at 700°C for 16 hours, 10.3 percent. Ignition for 5 minutes at $1,200^\circ\text{C}$ gave complete conversion of the sample to β -dicalcium silicate and calcium oxide. Attempts to dehydrate the compound to tricalcium silicate were unsuccessful. Loss of water and liberation of free lime appear to take place concurrently.

In experiment 76 an attempt was made to prepare the hydrated tricalcium silicate from a $3\text{CaO}:1\text{SiO}_2$ mixture of β - $2\text{CaO}\cdot\text{SiO}_2$ and CaO treated with water at 250°C . The product consisted of calcium hydroxide and the granular dicalcium silicate hydrate obtained by Keevil and Thorvaldson [19] and also identified in experiment 65, table 8 of this paper.

(i) MOLAR RATIO CaO/SiO_2 , 4:1

Several experiments which were made to determine whether any hydrates richer in lime than $3\text{CaO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}$ exist are recorded in table 10.

TABLE 10.—Results of experiments on $4\text{CaO}:1\text{SiO}_2$ compositions

Experiment number	Starting material	Temperature	Pressure	Time		Product
				$^\circ\text{C}$	atm	
79	β - $2\text{CaO}\cdot\text{SiO}_2 + 2\text{CaO}$	250	39		7	$2\text{CaO}\cdot\text{SiO}_2\text{ aq} + \text{Ca}(\text{OH})_2$
80	$3\text{CaO}\cdot\text{SiO}_2 + \text{CaO}$	250	39		12	$3\text{CaO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}$
81	$1.4\text{CaO}:\text{SiO}_2\text{ aq} + 2.8\text{CaO}$	400	397		7	$3\text{CaO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O} + \text{Ca}(\text{OH})_2$
82	$1.3\text{CaO}:\text{SiO}_2\text{ aq} + 2.7\text{CaO}$	450	400		6	$3\text{CaO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O} + \text{Ca}(\text{OH})_2$

The results indicate that dicalcium and tricalcium silicates form the same hydrates as they did in the absence of excess lime. The dicalcium silicate hydrate formed in experiment 79 occurred in small irregular plates having refractive indices ranging from 1.62 to 1.64. It was the same product as was obtained in experiment 76, table 9, and experiment 65, table 8 of this paper.

5. CEMENTITIOUS MATERIAL IN SAND-LIME BRICK

Some experiments similar to those of Grime and Bessey [2] were made in an attempt to isolate the hydrated calcium silicate in a commercial sand-lime brick of good quality. Half of the brick was crushed in a porcelain mortar with as little grinding as possible. Of this material the sample passing a No. 40 sieve and retained on a No. 70 sieve after brief shaking was used. It contained 4.4 percent of soluble silica determined according to the usual procedure. The material was screened on a No. 200 sieve for $\frac{1}{2}$ hour and that passing was examined under the microscope. It appeared to consist almost wholly of calcite and was discarded. Screening was then continued another half hour. It was hoped by this method that the cementing material surrounding the sand grains might be rubbed off and concentrated. That this apparently occurred was shown by an increase in soluble silica to 16.2 percent in the material passing the No. 200 sieve. A number of pennies were then added to the material on the No. 200 sieve to assist the rubbing action, and the screening was continued for an hour. The material passing then showed a soluble silica content of 20.2 percent. However, in the X-ray patterns of both samples only the lines of calcite and quartz appeared.

It was thought that evidence of the presence of a crystalline hydrated calcium silicate might be obtained using a laboratory-prepared brick. For this purpose a mixture of 10 percent of hydrated lime and 90 percent of graded Ottawa sand (containing 0.13 percent of soluble silica) was molded into a bar in a hand press. The bar was then treated in contact with water at 175° C for 20 hours. After crushing the brick, the whole sample was found to contain 2.6 percent of soluble silica. This sample was rubbed with the fingers on a No. 20 sieve and the material passing in each case was rubbed successively on the No. 48, 100, and 200 sieves. The material passing the No. 200 sieve contained 16.8 percent of soluble silica. In the X-ray pattern the strongest lines were those of calcium hydroxide together with the lines of quartz.

Another bar was treated in the bomb at 175° C for 15 days. After a separation similar to that just described the material passing a No. 200 sieve was extracted for 75 hours with boiling ethylene glycol in an extractor of the type used in rubber analysis. The residue contained no free calcium hydroxide. Its X-ray pattern showed the lines of quartz with a few additional lines of moderate intensity which did not coincide with any of the lines of quartz, calcite, or calcium hydroxide. It was not possible, however, to assign these additional lines with certainty to any of the known hydrated calcium silicates.

IV. DISCUSSION

In the manufacture of sand-lime brick a wetted mixture of about 10 percent of hydrated lime and 90 percent of sand is pressed into forms, the resulting blocks removed, and steamed in an autoclave at 150° to 200° C (5 to 15 atm) for 8 to 12 hours. The nature of the cementing material formed by this treatment has never been established, but it is presumed to be a hydrated calcium silicate. X-ray and optical data [2] indicate that it may be amorphous. Some inferences regarding its potential crystalline composition may, however, be made from the results of this paper.

Lime usually constitutes only about 10 percent of the sand-lime brick mix, but its proportion to surface silica available for reaction will evidently be much higher owing to the relative coarseness of the sand particles. Thus, it is probable that the cementing material of the brick will be much richer in lime than the mix as a whole. Such a condition might permit the crystallization of compounds as highly basic as $10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$. This compound appears to be by far the most easily formed of the hydrated calcium silicates at the temperatures employed in sand-lime brick manufacture. However, if the lime available for reaction with surface silica is insufficient to form this compound the potential crystallization of a less basic compound such as gyrolite might be favored.

Although the experiments with sand-lime brick failed to establish the identity of the cementing material in sand-lime brick, the greatly increased soluble silica content of the finer fractions of the crushed brick appears to indicate the formation of potentially crystalline compounds. That these combinations could not be identified by their X-ray patterns is not surprising in view of the fact that the various syntheses described in this paper all required much longer periods of time than those employed in sand-lime brick manufacture. The appearance of additional lines in the X-ray pattern of the sand-lime brick treated for a longer period is promising, and it is hoped that further work may reveal their source.

The crystalline materials obtained by reaction of water on β -dicalcium silicate and tricalcium silicate at room temperature are noteworthy with reference to end products in the setting of portland cement. There is a possibility that the product derived from dicalcium silicate, and which had a composition approximating $3\text{CaO}\cdot 2\text{SiO}_2\cdot 1.5\text{H}_2\text{O}$ on complete crystallization, may occur in set portland cement. This product could not be identified with any of the known calcium hydrosilicate minerals.

The poorly crystallized material which resulted from treatment of tricalcium silicate with water at room temperature had a CaO/SiO_2 molar ratio of only 1.3 owing to the extensive hydrolysis which had taken place in the presence of a large excess of water. Therefore, it probably would not form in the setting of portland cement when less water is used but might occur in hydrated puzzolanic cement where the proportion of silica to lime is higher. Unfortunately, the pattern of this material also could not be identified.

As has been pointed out by Thorvaldson and coworkers [17, 18, 19], the compounds designated in this paper as $10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$ and $3\text{CaO}\cdot \text{SiO}_2\cdot 2\text{H}_2\text{O}$ are probable products of the autoclave treatment of portland cements. Under such conditions it has also been

shown by Mather and Thorvaldson [20] that tricalcium aluminate will hydrate to $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ and tetracalcium aluminoferrite to $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ and $\text{CaO}\cdot\text{Fe}_2\text{O}_3$ hydrate, which, in turn, will slowly decompose to $\text{Ca}(\text{OH})_2$ and hematite. Thus it would appear possible to hydrate cement partially in the autoclave without the liberation of appreciable free lime. This is actually the case. A group of four high-tricalcium silicate cements all having ignition losses and free-lime contents of less than 1 percent was steamed in the autoclave at 200°C (15 atm) overnight. The ignition loss in each case was increased to 5 to 6 percent. The free-lime content of one cement remained the same, another showed a slight decrease, and the two remaining, an increase of a few tenths of a percent.

With regard to the 215°C autoclave test [1] for neat cement bars, the fact that calcium hydroxide can react with amorphous hydrated calcium silicate already formed, to give the hydrate of tricalcium silicate, is significant. This result, taken in conjunction with those of Mather and Thorvaldson [20], indicates that any expansion which results from autoclaving cannot be caused by crystallization of calcium hydroxide liberated from the cement compounds, but must be ascribed to other causes.

As was pointed out with reference to sand-lime brick, the crystallization of hydrated calcium silicates occurs slowly, requiring days or weeks to reach completion even at temperatures above 200°C . It is not to be expected, therefore, that well-developed crystals of any of the various hydrates described in this paper would be found in specimens steamed for the short period employed in the autoclave test. Only incipient crystallization would occur, but the products should be the same as those formed over longer periods.

V. SUMMARY

Table 11 gives a summary of optical properties of the natural and synthetic minerals identified in this investigation.

X-ray study of the hydrated calcium silicate minerals indicated that the following are distinct compounds:

Okenite.....	$\text{CaO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$.
Gyrolite.....	$2\text{CaO}\cdot 3\text{SiO}_2\cdot 2\text{H}_2\text{O}$.
Crestmoreite.....	$2\text{CaO}\cdot 2\text{SiO}_2\cdot 3\text{H}_2\text{O}$.
Xonotlite.....	$5\text{CaO}\cdot 5\text{SiO}_2\cdot \text{H}_2\text{O}$.
Afwillite.....	$3\text{CaO}\cdot 2\text{SiO}_2\cdot 3\text{H}_2\text{O}$.
Foshagite.....	$5\text{CaO}\cdot 3\text{SiO}_2\cdot 3\text{H}_2\text{O}$.
Hillebrandite.....	$2\text{CaO}\cdot \text{SiO}_2\cdot \text{H}_2\text{O}$.

Centrallasite, $4\text{CaO}\cdot 7\text{SiO}_2\cdot 5\text{H}_2\text{O}$, and truscottite, $4(\text{Ca},\text{Mg})\text{O}\cdot 7\text{SiO}_2\cdot 5\text{H}_2\text{O}$, seem to be impure forms of gyrolite. Riversideite, $2\text{CaO}\cdot 2\text{SiO}_2\cdot \text{H}_2\text{O}$, is apparently not a distinct mineral and is probably the same compound as crestmoreite.

Preparations having X-ray patterns identical with those of gyrolite, xonotlite, and foshagite were synthesized by hydrothermal methods. Other compounds formed were cristobalite, wollastonite, pseudowollastonite, $\beta\text{-}3\text{CaO}\cdot 2\text{SiO}_2$, $4\text{CaO}\cdot 5\text{SiO}_2\cdot 5\text{H}_2\text{O}$, $\text{CaO}\cdot \text{SiO}_2\cdot \text{H}_2\text{O}$, $2\text{CaO}\cdot \text{SiO}_2\cdot \text{H}_2\text{O}$, $10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$, and $3\text{CaO}\cdot \text{SiO}_2\cdot 2\text{H}_2\text{O}$.

TABLE 11.—Optical properties of natural and synthetic minerals identified in this study

Composition	Optical properties					Crystal system and habit	Elongation	Mineral name	Obtained synthetically
	Sign	Optic angle	α or ω	β	γ or ϵ				
CaO.2SiO ₂ .2H ₂ O	—	Large	1.530		1.541	Orth. fibrous.	+	Okenite	No.
2CaO.3SiO ₂ .2H ₂ O	—	0	1.548		1.536	Trig. fibrous lamellae.	+	Gyrolite	Yes.
4CaO.5SiO ₂ .5H ₂ O				1.54		Acicular	+	Tobermorite(?)	Yes.
5CaO.5SiO ₂ .H ₂ O	+	Small	1.583	1.583	1.594	Orth. (?) fibrous.	+	Xonotlite	Yes.
CaO.SiO ₂ .H ₂ O				1.603		(?)	—		Yes.
2CaO.2SiO ₂ .3H ₂ O	—	Large	1.593	1.603	1.607	Fibrous	+	Crestmoreite	No.
3CaO.2SiO ₂ .1.5H ₂ O				1.60		do			Yes.
3CaO.2SiO ₂ .3H ₂ O	+	54°	1.617	1.620	1.634	Mon. prism.	—	Afwillite	No.
5CaO.3SiO ₂ .3H ₂ O	+	Small	1.594	1.594	1.598	Orth. fibrous.	+	Foshagite	Yes.
2CaO.SiO ₂ .H ₂ O	—	60° to 80°	1.605	1.61	1.612	do	+	Hillebrandite	No.
2CaO.SiO ₂ .H ₂ O				1.60		(?)	+		Yes.
2CaO.SiO ₂ .H ₂ O				1.64		(?)			Yes.
10CaO.5SiO ₂ .6H ₂ O	+	Medium	1.614	1.620	1.633	Orth.	+		No.
6CaO.3SiO ₂ .2H ₂ O			1.642		1.672	(?)			Yes.
3CaO.SiO ₂ .2H ₂ O			1.590		1.602	Fibrous	+		Yes.

Attempts to produce okenite synthetically were unsuccessful. Thus, a sample of calcium disilicate glass treated with water for 8 weeks at 150° C gave partial crystallization to cristobalite only.

Gyrolite was formed at 150° to 400° C from glasses and amorphous hydrates having CaO/SiO₂ molar ratios in the vicinity of 2:3.

Treating amorphous hydrate with CaO/SiO₂ molar ratio 0.80 at temperatures between 150° and 275° C gave a single phase of distinctive X-ray pattern, and a composition corresponding to 4CaO.5SiO₂.5H₂O. This composition is similar to that reported for the rare mineral tobermorite. At 300° C the product was xonotlite.

Amorphous monocalcium silicate hydrate at 150° C crystallized to CaO.SiO₂.H₂O, which had a distinctive X-ray pattern. However, in the presence of higher molar ratios of lime to silica, CaO.SiO₂.H₂O was formed at temperatures as high as 350° C.

Xonotlite, 5CaO.5SiO₂.H₂O, crystallized from preparations of amorphous hydrated monocalcium silicate between 165° ± 15° C and 395° ± 5° C (70 to 225 atm). Above 395° C wollastonite crystallized.

Amorphous hydrate of molar ratio 3CaO/2SiO₂ treated between 150° and 400° C did not yield afwillite, 3CaO.2SiO₂.3H₂O, but instead crystallized partially to CaO.SiO₂.H₂O at the lower temperatures and to xonotlite at the higher. These were probably metastable crystallizations resulting from the relatively high crystallization potential of the monocalcium silicate hydrates. Anhydrous tricalcium disilicate treated at 250° C was converted to an unidentified hydrate.

The usual form of anhydrous tricalcium disilicate treated at 500° C (380 atm) for 2 weeks was converted to a low-temperature or β form of the anhydrous compound. It inverts to the high-temperature form at 1,024° ± 5° C.

Glass of composition 5CaO.3SiO₂ treated at 300° and 350° C was converted to a product having an X-ray pattern identical with that of the mineral foshagite.

The compound $10\text{CaO}\cdot 5\text{SiO}_2\cdot 6\text{H}_2\text{O}$ was formed from β - and γ -dicalcium silicates, tricalcium silicate, and mixtures of lime and silica gel in the temperature range 100° to 200° C. Attempts to prepare a hydrate identical with natural hillebrandite were unsuccessful.

Tricalcium silicate treated with water between 200° and 450° C hydrated directly to $3\text{CaO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}$. No hydrates of higher lime content than $3\text{CaO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}$ appear to exist.

A number of unsuccessful attempts were made to isolate and identify the cementing material in sand-lime brick.

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“The Hydration of Alite: A Time-Resolved Quantitative X-Ray Diffraction Approach Using the G-Factor Method Compared with Heat Release,” Jansen, D., S. T. Berghold, F. Goetz-Neunhoeffler, and J. Neubauer, *J. Appl. Cryst.*, 44, 895-901, 2011.

The hydration of alite: a time-resolved quantitative X-ray diffraction approach using the G-factor method compared with heat release

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The classical external-standard method derived from the work of O'Connor & Raven [*Powder Diffr.* (1988), 3, 2–6] was used to examine the hydration of the major phase, alite, of ordinary Portland cements at different temperatures and different water/alite ratios. In order to estimate the accuracy of the method, heat-flow curves were calculated from the alite dissolution curves obtained from X-ray diffraction *in situ* experiments. The heat-flow curves calculated in this way were compared with heat-flow curves recorded using a calorimeter. It is shown that the calculated curves agree well with the curves obtained from heat-flow experiments.

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1. Introduction

Even though ordinary Portland cements (OPCs) have been used and studied for decades, the hydration kinetics of their major phase, alite (doped tricalcium silicate, C_3S), are still not completely understood. Several theories have persisted alongside each other. The major concern of these theories has been to explain the reaction kinetics of alite hydration which are commonly determined from heat-flow calorimetric measurements (Fig. 1). An initial heat flow can be detected directly after mixing (I). This is followed by a period of slow reaction which is known as the induction period (II). This induction period is followed by the main hydration reaction (III), which is separated into the acceleration (IIIa) and the deceleration period (IIIb). The main hydration reaction is normally completed after the elapse of 24 h, but the hydration continues at low heat-flow levels for months. The hydration

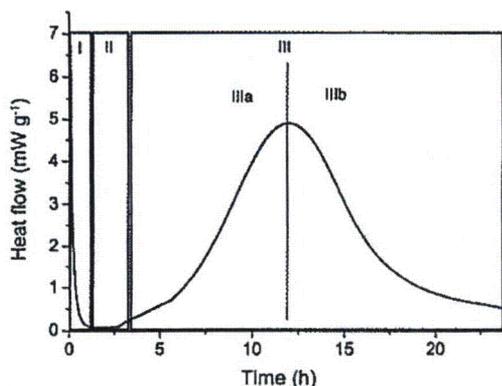
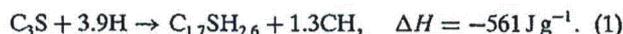


Figure 1
Heat-flow curve of alite; water/alite ratio = 0.5; $T = 296$ K.

results in the formation of an amorphous calcium–silicate–hydrate (C–S–H) gel and crystalline portlandite. The Ca/Si ratio of C–S–H depends on the temperature (Escalante-Garcia & Sharp, 1999), on the water-to-cement ratio (Locher, 1967) and, in the case of an OPC, on the composition of the OPC used (Richardson, 1999). After 28 d, the Ca/Si ratio of a C–S–H gel formed in a hydrated OPC at 293 K with a water-to-cement ratio of 0.4 stands at 1.7, according to Allen *et al.* (2007). We thus arrive at equation (1) for the hydration of C_3S after this point in time:



The enthalpy of reaction ΔH is the difference between the sum of the formation enthalpies of the products ($\Delta H_{F, \text{products}}$) and the sum of the formation enthalpies of the reactants ($\Delta H_{F, \text{reactants}}$).

The enthalpy for equation (1) was calculated using data acquired by means of the thermodynamic software GEMS (Kulik, 2010) using the GEMS version of the Nagra/PSI thermodynamic database (Hummel *et al.*, 2002; Thoenen & Kulik, 2003), the cemdata07 database (Lothenbach *et al.*, 2008) and the enthalpy of formation for $C_{1.7}SH_{2.6}$ derived following Fuji & Kondo (1983).

The most widely used theory for the hydration of alite predicts the formation of a metastable protective C–S–H layer on the C_3S grain surface directly after wetting. This protective layer suppresses further hydration of the C_3S and ends the initial period (Stein & Stevels, 1964; Gartner & Gaidis, 1989). At the end of the induction period, this protective layer is destabilized, giving rise either to a more permeable layer or to the dissolution of the layer, which allows the hydration reaction to start again. Livingston *et al.* (2010) assume, from the results of their nuclear resonance reaction analysis of C_3S

hydration, that an existing protective layer breaks because of the osmotic pressure attained between the silicate-rich grain surface and the calcium-rich solution.

Another theory does not require this assumption of the emergence of a protective layer in order to explain the progress of alite hydration. For example, Garrault & Nonat (2001) and Peterson & Whitten (2009) assume that a single process is responsible for both the nucleation and the growth of C-S-H, which begins, according to Rodgers *et al.* (1988), directly after mixing. Thomas (2007) concludes, from mathematical calculation of a boundary nucleation and growth model, that the hydration continues at low levels during the period of slow reaction. This, he suggests, is because there are only a small number of C-S-H nucleons present, so that this period does not form a separate chemical process in itself. Assuming a constant rate for the C-S-H nucleation process (Thomas, 2007), the acceleration period would begin once a sufficient number of C-S-H nucleons have been precipitated. Juilland *et al.* (2010) suggest that there are different solution mechanisms working at different degrees of undersaturated solution, as described by Lasaga & Lutge (2001) for several minerals.

At a certain point, the hydration of alite becomes diffusion controlled, because the unreacted alite grains come to be covered by a continuous product layer. Some authors (*e.g.* Garrault & Nonat, 2001) claim that the diffusion regime has already begun with the onset of the deceleration period, while others consider it to begin only with the end of the deceleration period, when the hydration has reached very low levels, or at even later points in time (Thomas *et al.*, 2009).

X-ray diffraction (XRD) *in situ* analysis is a suitable method for examining the phase development of hydrating alite/water mixtures during the process of hydration. This is the case even though the C-S-H phase that is formed during this process is not detectable by X-ray diffraction in the first 24 h because of its low degree of crystallinity. Besides this, the water added to the alite cannot be quantified directly with X-rays.

Software for Rietveld (1969) refinement usually gives the total of the crystalline phases determined, normalized to 100 wt% (ZMV algorithm; Hill & Howard, 1987). In cases where amorphous phases are present (in the case of alite/water mixtures, there is likely to be at least C-S-H phase and water) the amounts of the crystalline phases calculated from Rietveld analysis will differ from the actual amounts. Moreover, any computing error of any phase of the mixture will have an influence on the calculated amounts of all phases in the mixture.

There exists the possibility of plotting peak areas or peak intensities in order to show phase developments in pastes in quantitative terms (Pöllmann *et al.*, 2009; Pelletier *et al.*, 2009) and without normalization to 100 wt%. Unfortunately it is not possible to calculate actual quantities, given in wt% of the alite/water mixture, by this method.

An internal-standard method can be applied in order to establish the phase composition of the crystalline phases as well as the amount of the amorphous content of an alite/water mixture (Scrivener *et al.*, 2004). If an internal standard is

added to the cement, there exists the possibility of the standard material exerting an influence on the hydration of the cement.

Westphal *et al.* (2009) have examined the mathematical consequences of the internal-standard method and have concluded that there is such a thing as an optimal amount of internal standard that can be added to the sample. Assuming an amorphous content of 35 wt% on average in the first 22 h of hydration (depending on the C-S-H phase and water/alite ratio), the most advisable option, they propose, is to work with an amount of internal standard of at least 40 wt%. Where this is not done, the user will have to accept a considerable analysis error. Such a high amount of internal standard might possibly have an influence on the hydration inasmuch as it might bring about alterations in nucleation and growth kinetics or the water/alite ratio.

In order to avoid complications that might be caused by mixing an internal standard with the alite phase, we decided to make use of an external-standard method, which was first described by O'Connor & Raven (1988) but has not subsequently been used for the quantification of hydration reactions.

The scope set for this paper is to provide an answer to the question of whether or not XRD *in situ* analysis is a suitable method for characterizing the hydration process of the alite phase. It is also the intention of the authors to focus attention on the comparison between heat-flow curves as calculated from XRD data and heat-flow curves as measured from heat-flow experiments. The main focus is on the main hydration period of the cement, which sets in after several hours and is concluded within 24 h at room and higher temperatures.

However, a question that can be answered using XRD experiments is how the reaction from alite to portlandite and the C-S-H phase emerges. Assuming that there exist at least two processes here that release heat, namely the dissolution of the alite phase and the precipitation of portlandite and the C-S-H phase, it necessarily follows that dissolution and precipitation have to run synchronously in order to make it possible to calculate the heat flow using only the dissolution curve of the alite phase obtained from Rietveld analysis.

2. Materials and methods

Alite was synthesized using CaCO₃, Al₂O₃ and SiO₂ from Alfa Aesar and MgO from Merck. Al₂O₃ and MgO were added to stabilize a monoclinic (*M3*) alite structure (De La Torre *et al.*, 2002). The chemicals were homogenized in a vibration disc mill and placed in platinum crucibles. The thermal treatment was carried out three times at a temperature of 1673 K for 4 h in a chamber furnace. The synthesized alite was checked for phase purity using XRD. The specific surface of the synthesized alite was measured to be 0.29 m² g⁻¹, using the Blaine method.

For the *in situ* XRD analysis a custom-made sample holder with a heater/cooler unit was used (Hesse *et al.*, 2008). Cement and water were mixed by external stirring for 1 min. The paste was then put into the sample holder and covered by a 7.5 µm-

Table 1
Structure models used for Rietveld refinements.

Phase	ICSD code	Author
Alite	94742	De La Torre <i>et al.</i> (2002)
Silicon	51688	Többsen <i>et al.</i> (2001)
Portlandite	34241	Greaves & Thomas (1986)

Table 2
Chemical composition of the samples (wt%).

CaO	71.8
Al ₂ O ₃	0.6
SiO ₂	25.9
MgO	1.8

thick Kapton polyimide film. The diffraction patterns were recorded using a D8 diffractometer (Bruker) equipped with a LynxEye position-sensitive detector. We made use of Cu K α radiation at 40 kV and 40 mA, and recorded from 7° 2 θ to 40° 2 θ with a step width of 0.0236 and 0.58 s counting time per step. Under these conditions, it is possible to record 88 ranges within the first 22 h of hydration. For the Rietveld refinements, the program *Topas* version 4.2 from Bruker AXS Inc. (Madison, Wisconsin, USA) (fundamental parameters approach) was used. There was no evidence for any difference in the results when working with a longer range from 7° 2 θ to 70° 2 θ .

The quantitative phase composition of the alite paste was determined using the *G*-factor method, which was first described by O'Connor & Raven (1988) and which has already been used successfully for the examination of cements and cement pastes (Jansen, Goetz-Neunhoffer *et al.*, 2011; Jansen, Stabler *et al.*, 2011). In addition, the method was recommended by Schreyer *et al.* (2011) for the examination of organic mixtures. For this purpose, a well known standard (in our case silicon; Jansen, Stabler *et al.*, 2011) is used in order to calculate the *G* factor [equation (2)]:

$$G = s_{\text{Si}} \frac{\rho_{\text{Si}} V_{\text{Si}}^2 \mu_{\text{Si}}^*}{c_{\text{Si}}}, \quad (2)$$

where s_{Si} is the Rietveld scale factor of silicon from Rietveld analysis, ρ_{Si} the density of silicon, V_{Si} the unit-cell volume of silicon, c_{Si} the weight fraction of silicon (100 wt%) and μ_{Si}^* the mass attenuation coefficient of silicon.

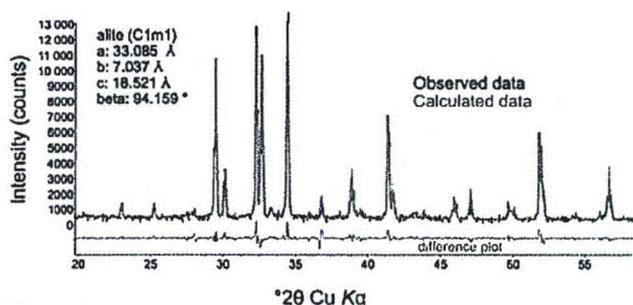


Figure 2
Rietveld refinement of a powder pattern of the synthesized alite.

Table 3
Mass attenuation coefficients (MAC) (cm² g⁻¹) of the samples.

MAC _{dry alite}	99
MAC _{H₂O}	10.2
MAC(alite/water paste; water/alite ratio = 0.5)	69.4
MAC(alite/water paste; water/alite ratio = 1)	54.6

Table 4
Computed *G* factor and structural details regarding the silicon standard employed.

Scale factor from Rietveld refinement	0.007695
Cell volume	1.6 × 10 ⁻²² cm ³
Density	2.33 g cm ⁻³
Mass attenuation coefficient	63.7 cm ² g ⁻¹
<i>G</i> factor	2.92 × 10 ⁻⁴⁴ cm ⁵ per wt%

The *G* factor was then used to determine the mass concentration of each crystalline phase *j* in the hydrating alite paste [equation (3)]:

$$c_j = s_j \frac{\rho_j V_j^2 \mu_{\text{sample}}^*}{G}. \quad (3)$$

This made it imperative that the sample be measured under the same conditions as the standard. Since the alite paste was covered during the measurement process with a Kapton film, which can cause absorption of X-rays and thereby intensity loss, it was necessary that the standard material be likewise covered with a Kapton film during its measurement process. The structure models and the respective ICSD codes are shown in Table 1. The chemical composition of the alite samples is shown in Table 2. The mass attenuation coefficients of the dry alite powder and the pastes are shown in Table 3. Mass attenuation coefficients for the various elements were drawn from *International Tables for Crystallography* (Prince, 2004). The mass attenuation coefficient of the alite powder was calculated from the chemical composition. More details about the standard used are shown in Table 4. The *G* factor was evaluated from six powder samples with individual preparations. The mean value of all measurements was used for the quantification of the water/alite pastes. The standard deviation of the mean value for the scale factor of the silicon powder was 0.8 wt%.

The *G*-factor method of O'Connor & Raven (1988) displays enormous advantages where it is applied to the quantification of alite hydration. Where this method is adopted, the crys-

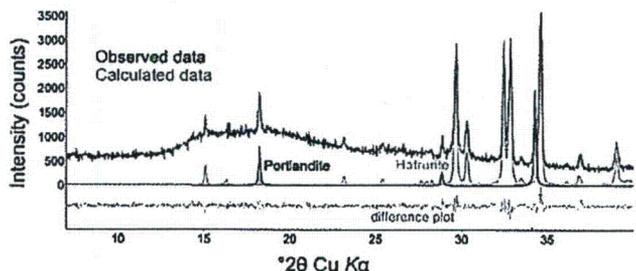


Figure 3
Rietveld refinement of a paste after 11 h hydration; water/alite ratio = 0.5; *T* = 310 K.

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talline phases can be quantified directly from the scale factors. No error in the determination of any individual phase has any influence on the determined amounts of the other phases. In addition, the amorphous phases, namely water and the C-S-H

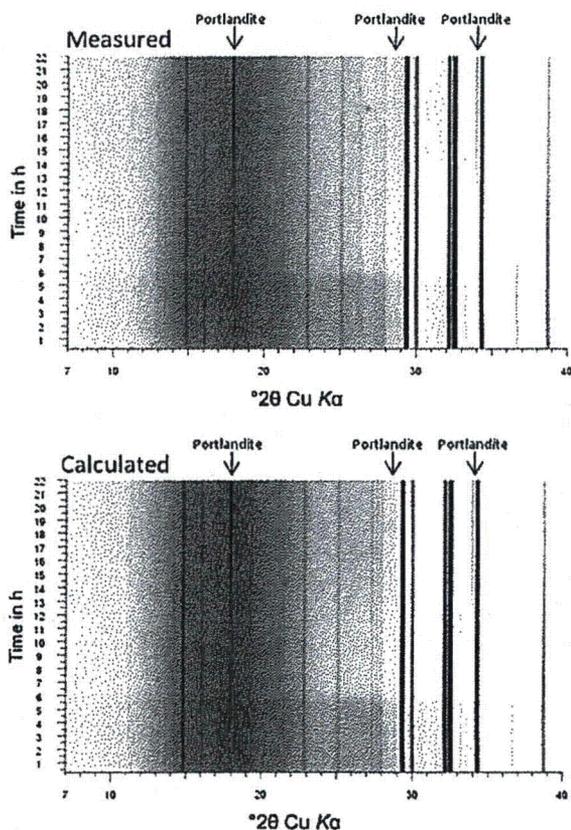


Figure 4
Level plots of all patterns measured and calculated for the system at 296 K and a water/alite ratio of 0.5. (Portlandite peaks are marked, the remaining peaks are alite peaks.)

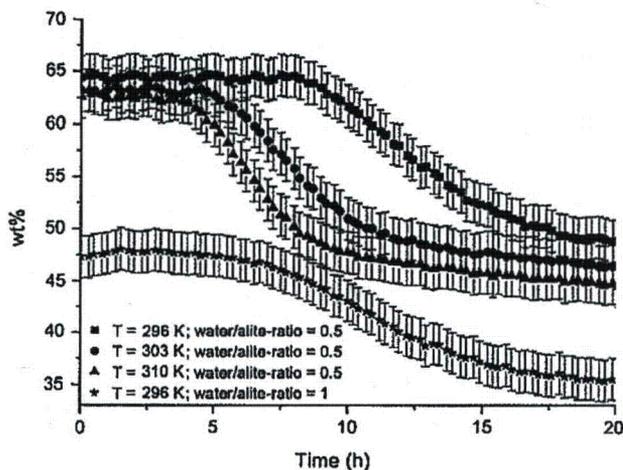


Figure 5
Content of alite in different alite/water pastes during the process of hydration.

phase, cannot be quantified using the standard Rietveld ZMV algorithm, which only considers the crystalline phases.

Heat-flow experiments were carried out using a commercial TAM Air calorimeter. Alite and water were equilibrated before the measurements in a calibrated heat chamber. Mixing of the alite with the water was carried out externally by means of a special mixer which allows reproducible stirring for 1 min. The samples were then put in the calorimeter. The first half-hour of the heat-flow experiments cannot be evaluated because of the disturbance of the signal caused by opening the calorimeter.

Heat-flow curves were calculated from the *in situ* XRD results (alite dissolution curves) using equation (4) (modified from Hesse *et al.*, 2011):

$$HF = \frac{\partial \text{wt}\% \text{ alite} / \partial t}{100} \frac{\Delta HR}{3.6} (-1), \quad (4)$$

where $\partial \text{wt}\% \text{ alite} / \partial t$ is the derivation of the alite curve from XRD *in situ* experiments, and ΔHR is the enthalpy of reaction of equation (1).

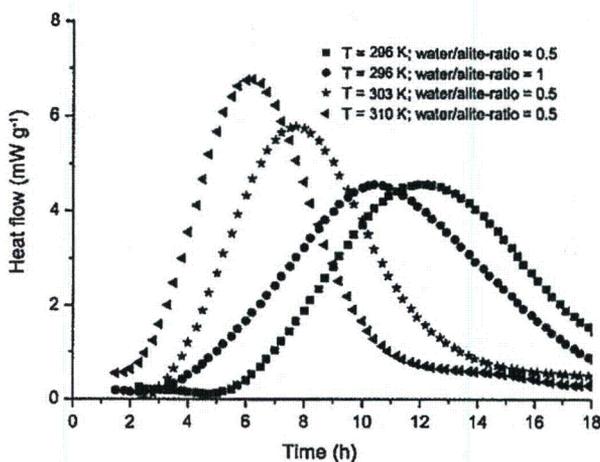
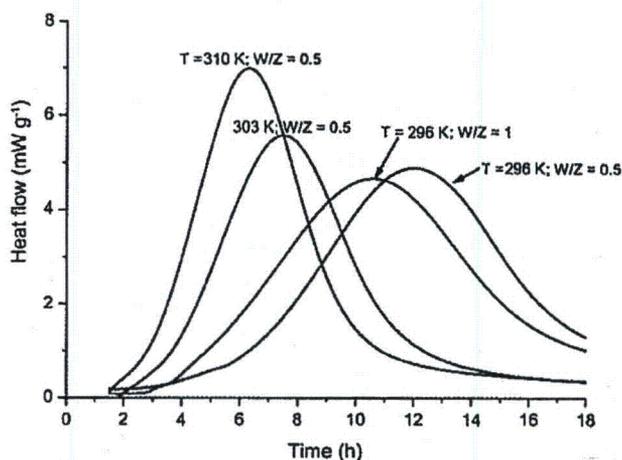


Figure 6
Measured heat flows (top) and calculated heat flows (bottom) of the alite/water pastes at different temperatures and water/alite ratios (from 1.5 h).

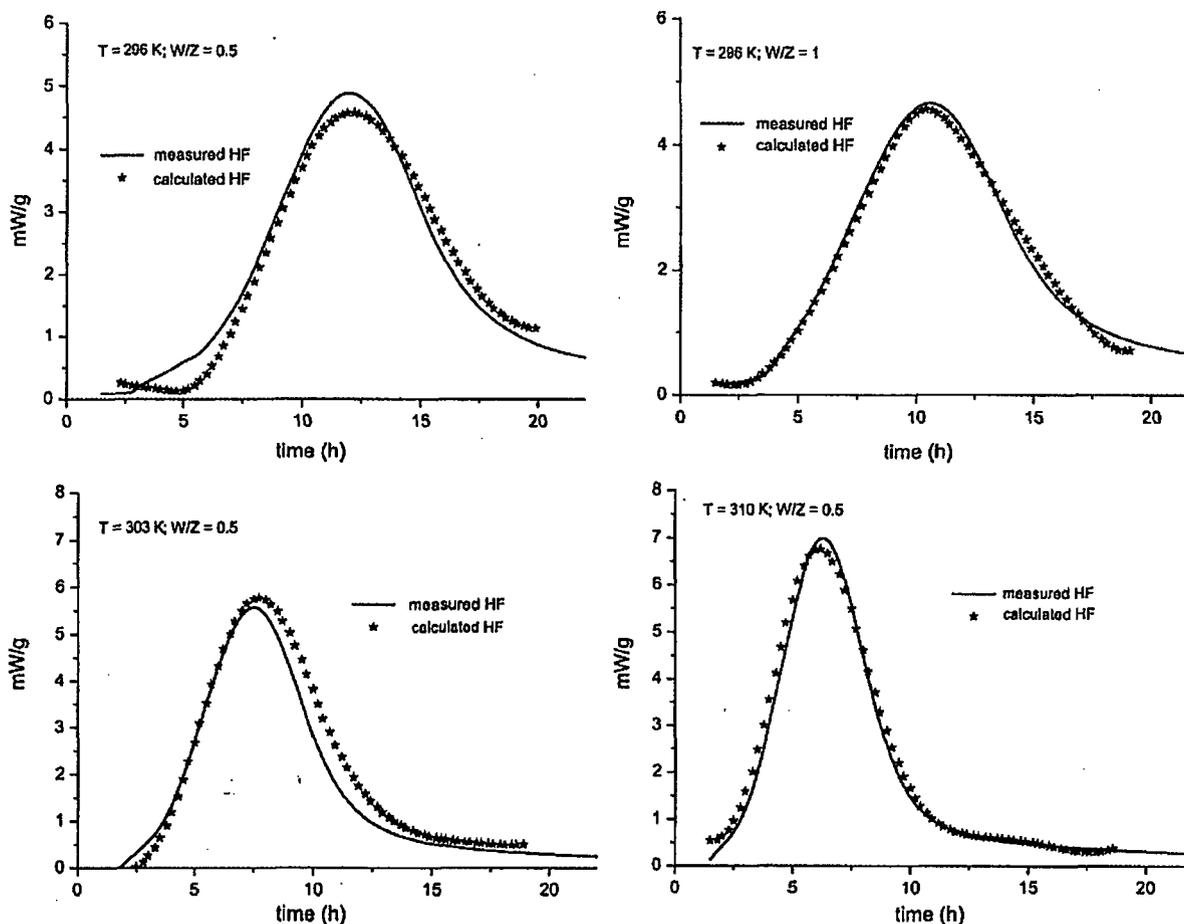


Figure 7
Comparison between measured and calculated heat flows of synthetic alite at different temperatures and water/alite ratios (from 1.5 h).

3. Results

The Rietveld refinement of the synthesized alite is shown in Fig. 2.¹ There was no sign of any phase except the alite phase. The calculation of the amount of alite using the G factor, which was derived from the standard material silicon, resulted in 96 (2) wt% of alite in our sample and 4 (2) wt% of amorphous or non-fitted phase. We assume that the structures used, as well as inaccurate dislocation parameters, might possibly be the reasons for the underquantification of the alite phase (Jansen, Stabler *et al.*, 2011). An amorphous, glassy phase is not verified.

The Rietveld refinement of the hydrating alite/water paste is shown in Fig. 3. There is close agreement between the intensity as observed and the intensity as calculated. The hump between $15^\circ 2\theta$ and $25^\circ 2\theta$ is created by the Kapton foil which covered the sample in order to avoid interaction with atmospheric CO_2 or water loss. The background of the Kapton foil and the water was considered using a special peaks phase model (Hesse *et al.*, 2009).

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: CG5188). Services for accessing these data are described at the back of the journal.

Fig. 4 shows level plots of all patterns calculated and measured for the system at 296 K and a water/alite ratio of 0.5 as a function of time, representative of all measurements performed and refined. All Rietveld refinements were as good as the refinement shown in Fig. 4.

The results from the XRD *in situ* experiments are shown in Fig. 5. It can be seen that the reaction of the alite phase strongly depends on both the temperature and water/alite ratio. Since about 96 wt% of crystalline alite could be detected in the dry sample, we can expect an absolute alite content of around 64 wt% in the cement paste, when working with a water/alite ratio of 0.5. A water/alite ratio of 1 would result in an amount of 48 wt% of alite in the paste, assuming that no alite reacts immediately after mixing the alite with water. Fig. 5 shows that no dissolution of the alite phase directly after mixing could be proven by means of the G -factor method. This leads us to the conclusion that either no alite reacts immediately with water or only very low amounts of alite are dissolved immediately, the amounts being lower than the standard deviations of the results of our experiments (± 2 wt%).

The heat-flow curves as measured and the heat-flow curves as calculated from XRD data using equation (4) are shown in

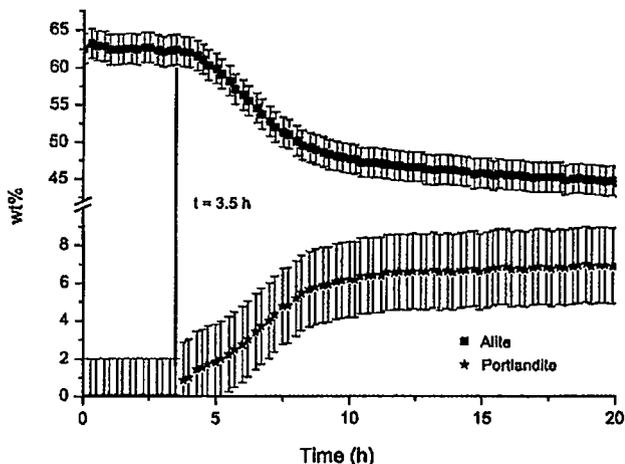


Figure 8
Quantitative phase development of alite and portlandite during the hydration of alite and water (water/alite = 0.5, $T = 310$ K).

Fig. 6. It can be seen that the calculated heat-flow curves accord to a great extent with the measured heat-flow curves. It is a fact that slow reactions are much harder to track by X-ray experiments than fast reactions. Therefore it is not surprising that the main period of the hydration is much easier to reproduce by means of X-ray diffraction than is the induction period.

The direct comparison of the curves is shown in Fig. 7. There is close agreement between the heat-flow curves as measured and the calculated heat-flow curves evaluated using the determined alite content measured by X-ray diffraction. It can be proven that the heat-flow curve obtained from the heat-flow experiments can be explained by the hydration reaction of the alite phase. This leads us to the conclusion that the quantification method chosen for the experiments can be recommended for the quantification of hydration reactions, such as the reaction of alite with water.

The fact that the complete hydration reaction [equation (1)] can be described by the alite dissolution curve can be interpreted in two ways. The first is that all heat is released during the dissolution of the alite phase. The precipitation of portlandite and the C-S-H phase does not contribute to the heat flow that can be detected from heat-flow experiments.

Another, more likely, explanation is that the dissolution of alite and the precipitation of portlandite and the C-S-H phase take place synchronously. This makes it conceivable that the heat-flow curve of alite with water is correctly described by the dissolution of alite.

A plot of the alite curve and the portlandite curve in the same diagram also shows that the dissolution of the alite phase and the precipitation of the portlandite phase emerge synchronously. Fig. 8 shows both curves at a water/alite ratio of 0.5 and at a temperature of 310 K, representative of all experiments performed. Under these conditions, the dissolution of alite and the precipitation of portlandite begin at a point in time some 3.5 h after mixing of the reactants.

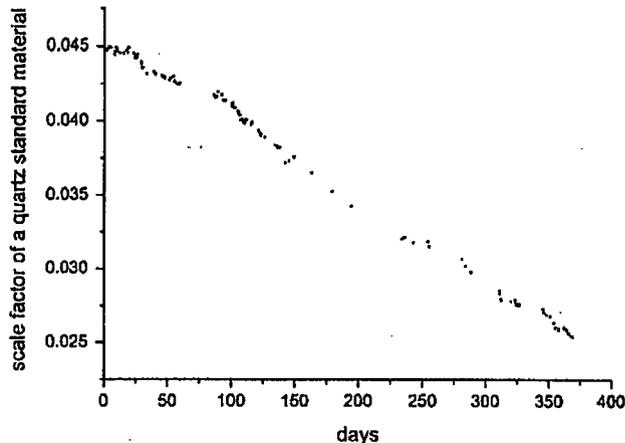


Figure 9
Development of the scale factor of a quartz standard material over time.

4. Conclusion

The method presented by O'Connor & Raven (1988) was a crucial step in developing a method for quantifying materials with amorphous portions. The implementation of this method for the characterization of hydration processes turned out to be very promising. It transpires that the calculation of a calibration factor G is of great practical use in the day-to-day work of a laboratory where hydration processes of materials containing crystalline phases are under examination.

It could be shown that the dissolution of alite, which was quantified by means of X-ray diffraction using the G -factor method, is suitable for characterizing the kinetics of the reaction of alite and water. The heat-flow curves obtained from heat-flow experiments could be simulated by using the quantitative XRD data for the calculation of heat-flow diagrams.

It is, however, imperative in every case that the user of the G -factor method always takes care to ensure that the right G factor is used. This is because the factor depends on the performance of the X-ray tube and the detector, and therefore strongly depends on time. As shown in Fig. 9, it is not advisable to calculate the G factor a long time before or after the point in time at which the experiment is actually performed.

The authors would like to thank Natalia Illenseer, Sebastian Klaus and Sebastian Scherb for their support during the experiments.

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WVMP SAR Reference 3-25

"A Study of Reaction between Calcium Oxide and Water," T. C. Miller, National Lime Association report, National Lime Association (Washington, DC), 1960.

AZBE AWARD No. 1

**A STUDY OF THE REACTION BETWEEN
CALCIUM OXIDE AND WATER**

BY

**T. C. MILLER, TECHNICAL DIRECTOR
INDUSTRIAL SALES DIVISION
NATIONAL GYPSUM COMPANY
BUFFALO, NEW YORK**

**(1960 Winner of the Victor J. Azbe Lime Award for the
Best Technical Paper on Lime)**

Published by

NATIONAL LIME ASSOCIATION

WASHINGTON 5, D. C.

FOREWORD

In 1960 Victor J. Azbe, President of the Azbe Engineering Corp., Clayton, Missouri, generously established through an irrevocable trust an annual award of \$1000 for the best technical paper on lime. Mr. Azbe, who has dedicated 40 years of his life as an international lime plant engineering consultant, hopes that this award will help stimulate greater interest in research on lime.

The National Lime Association -- administrator of this annual contest -- is pleased to publish the first award paper by T. C. Miller of the National Gypsum Company, which deals with the fundamental reaction between quicklime and water. If succeeding winning papers attain the high quality of Mr. Miller's, the lime industry will be the benefactor, and Mr. Azbe's generosity will be more than justified.

The Victor J. Azbe Lime Contest covers all aspects of lime manufacturing, including limestone processing, calcination, hydration, etc.; research on lime's physical and chemical properties; and methods of tests for evaluating lime's properties and quality. Further details of this contest can be obtained from the National Lime Association.

Robert S. Boynton, General Manager
National Lime Association
Washington 5, D.C.

A STUDY OF THE REACTION BETWEEN CALCIUM OXIDE AND WATER

By T. C. Miller
National Gypsum Co.

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I - INTRODUCTION

The reaction between calcium oxide (CaO) and water (H₂O) is an interesting and complex process. A great deal of confusion has existed in the use of calcium oxide by the chemical industry when it is required that the calcium oxide be converted to calcium hydroxide with water only, and oftentimes has resulted in unexpected results because of the unusual characteristics of such a calcium hydroxide. Commercial dry calcium hydroxide also has been criticized because of the varying degree of characteristics of a product from one producer. A study has been made of the reaction between calcium oxide and water for a wide range of variation in temperature to understand more fully the results to be expected when the reaction is carried out under specified conditions, from producing a dry product to that of producing suspensions with a large excess of water.

The physical analysis of products resulting from the dry hydration of calcium oxide under a variety of conditions indicates wide variations in settling time and specific surface or mean particle diameter. A similar study of aqueous suspensions of calcium hydroxide resulting from the wet slaking of calcium oxide in an excess of water under various conditions of temperature and concentration indicate that by this process of converting calcium oxide to calcium hydroxide a wide variation of settling times and specific surfaces is being obtained. Requests for the study of the process of a large number of chemical industries indicate the need for more technical knowledge of the hydration or slaking process and the resulting products. Results compiled from the study of industrial processes indicate the need for a search for a better understanding of conditions controlling the physical properties of calcium hydroxide and for better test methods which would more clearly define these physical properties.

It has been known for many years that the physical properties of settling rate and specific surface may vary over a relatively wide range with slight variations in a hydration process but these variations have never been studied in the effort to establish laws by which these variations take place. The data from industrial processes indicated that some law may exist by which these characteristics could be controlled and maintained. This paper deals with the results of such a study in slaking calcium oxide in an excess of water to produce aqueous suspensions of calcium hydroxide. It is not the intention at this time to include the results from a study of the dry hydration process.

It has been established during recent years that the specific surface of calcium hydroxide could be changed within certain limits by a change of either the concentration or the temperature of the water used for hydrating.

It is also known that there is correlation between specific surface and settling time of calcium hydroxide, but this correlation is not always in as close agreement as would be desired.

The cause for this disagreement has been studied with the result that physical limits have been established for standardizing the hydration of calcium hydroxide to produce the most desirable product available to increase the efficiency of a chemical process.

The single important fact to come from this study is the discovery of conditions that have given a clue to certain laws governing the control of particle diameter of calcium hydroxide resulting from the reaction of calcium oxide and water.

II METHODS OF EVALUATING THE PHYSICAL PROPERTIES OF CALCIUM HYDROXIDE

A Settling Time and Rate

The lack of understanding the physical properties of dry, as well as aqueous suspensions of calcium hydroxide has been primarily the result of the limited means of test methods. Since the introduction of commercial dry calcium hydroxide powder in 1904 the only test methods have been the settling time or rate determination and the sieve test. Although in use for an indeterminate number of years, the settling test did not become a standard test method until recently (A. S. T. M. C110-58). It is certainly a reliable and reproducible method of evaluation, but two major disadvantages make it difficult to become a popular test.

First, the time required to determine the settling time or rate on many types of calcium hydroxide, especially aqueous suspensions prepared by using an excess of water resulting in a slow settling product, make the test unsatisfactory as a control test. Second, when slight changes in the hydrating or slaking procedure are permitted, these changes influence a change in the viscosity of the suspension and consequently influence the settling time or rate. This gives the impression that changes in the quality of the calcium oxide are responsible for the differences in settling time or rate. Therefore, it appears that settling time tests of aqueous suspensions may require the determination of some other characteristic or characteristics to fully define the settling rate.

A sieve test is meaningless as far as defining a physical characteristic of calcium hydroxide is concerned. This test merely indicates the maximum size particle to which the calcium oxide has been slaked or the calcium hydroxide sieved or air separated. A sieve test gives no information on the size or distribution of particles finer than the finest sieve used.

A test method which would give more positive information in a short length of time has been desirable and is even in greater demand in present-day chemical processes where more definite physical characteristics are required. A study of various test methods has been undertaken over the years and very few have shown promise of becoming accepted methods for process control. Liquid elutriation methods employing water, methanol, ethanol and various other organic suspending mediums have been ruled out for the same reason that has made the settling time test so unpopular as a process-control test - - its time-consuming aspects.

Gas absorption methods are the most precise even for research work, but the cost of equipment and the high skill required for operation will undoubtedly prevent the method of being accepted as a control test.

B Specific Surface

During the past 15 years the Blaine air permeability method for specific surface has been employed as a method for studying the characteristics of calcium hydroxide. The results have been very encouraging. The method has been used throughout the present work and it is concluded that it is the most economical and rapid method for process control. The inexpensive apparatus makes it possible to provide more than one instrument for plant control where constant control must be maintained throughout more than one department. It is encouraging to cite that several of these testing instruments have been installed by industry for process-control testing. Approximately twenty to thirty minutes are required for testing a dry calcium hydroxide and approximately one and one-half hours for testing aqueous suspensions of calcium hydroxide.

The Blaine specific surface results are not influenced by viscosity or other physical properties. It is a test for the area exposed by one gram of calcium hydroxide which can be employed to calculate the theoretical mean particle diameter. The reader is referred to National Gypsum Company's Industrial Sales Department Technical Bulletin 2 BC for details of this method.

III METHODS OF HYDRATION

A Dry Hydration

The reaction between calcium oxide and water is not a simple one from any point of view. Calcium oxide is practically insoluble in water. Theoretically, 0.131 g dissolves in 100 ml water at 0° C and 0.07 g dissolves in 100 ml water at 100° C. Calcium oxide reacts with water to form calcium hydroxide. Calcium oxide is a member of a group of chemicals which liberates a considerable quantity of heat when reacting with water. This is known as an exothermic reaction. It is a remarkable property found in but a few materials which lime producers and consumers have failed to recognize to its fullest.

The reaction between calcium oxide and water takes place according to the equation



That is, 56.08 pounds of calcium oxide will react with 18.016 pounds of water to produce 74.096 pounds of calcium hydroxide. Each pound of calcium oxide will produce 1.3213 pounds of calcium hydroxide by combining with 0.3213 pound of water. The calcium hydroxide produced contains theoretically 75.7% calcium oxide and 24.3% water. Calcium hydroxide also is practically insoluble in water. The solubility at 0° C is 0.185 g per 100 ml of water and at 100° C is 0.077 g per 100 ml of water.

One significant property of this reaction is the liberation of 27,500 Btu of heat for each lb-mol (56.08 lbs) of calcium oxide. An idea of this amount of heat is illustrated by the fact that it is sufficient to raise the temperature of 194 pounds of water from 70° F to 212° F (boiling). Considering that only 18.016 pounds of water are theoretically required for each lb-mol of calcium oxide, a greater amount of heat is liberated than can be utilized with this amount of water simply to heat the product to 212° F and therefore the mass will become heated above 212° F unless a larger amount of water is used.

The extent of this exothermic reaction offers an opportunity to utilize the heat in three distinct methods of hydration according to the type of calcium hydroxide desired as determined by the utilization of this heat. These methods are outlined in Figure 1. The most familiar method of hydration used by commercial lime producers is the conventional one producing a dry powder at temperatures not exceeding 214° F. A second method produces

THE PRODUCTION OF CALCIUM HYDROXIDE FROM ROTARY KILN QUICKLIME

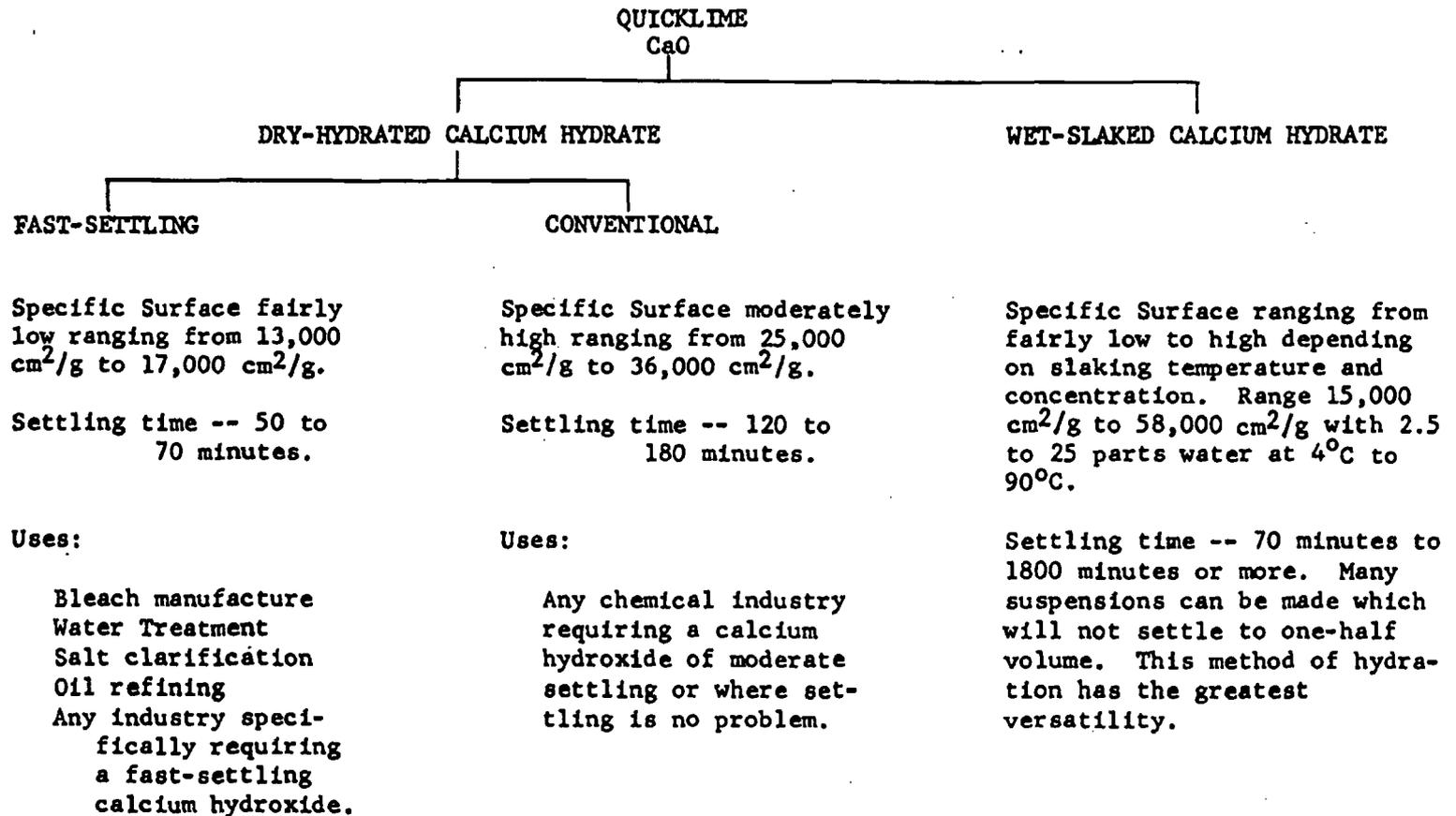


FIG. 1

a dry product at temperatures above 212° F by taking advantage of the liberated heat to control the size of calcium hydroxide particles. The third method of hydration, known more commonly as slaking, employs an excess of water to produce an aqueous suspension of calcium hydroxide. The chemical industry employs this method of producing calcium hydroxide principally because more economical equipment can be used and a greater latitude of variation is permissible with less skill. But recent studies of this method of producing calcium hydroxide indicate that closer controls are necessary to maintain constant physical properties of the calcium hydroxide.

1. Conventional Dry Hydrate

Commercial dry calcium hydroxide is normally produced by reacting approximately one pound of calcium oxide with 0.75 to 1.0 pound of water in a continuously agitated machine or hydrator. The mixture of CaO and H₂O, in the very early stages of hydration, produces a wet or "soupy" mass just prior to the beginning of the heat reaction. This mass reaches the temperature of boiling water within a few minutes when the excess water begins to be evaporated. The temperature cannot exceed the boiling point of water (212° F) at atmospheric pressure as long as liquid water (not water vapor alone) is present. The process is regulated with sufficient water to be assured that liquid water is present until the hydration reaction is practically complete. Then the last trace of liquid water is evaporated to produce a finely divided dry powder practically free of excess moisture.

The degree of burning a limestone to produce a quicklime influences to a great extent the type of calcium hydroxide which can be produced. A soft-burned quicklime reacts very readily with water as indicated by the temperature rise test involving a small amount of lime in a comparatively large amount of water. On the other hand, an overburned lime reacts much slower with water to give a low temperature rise by this test. Rotary kiln or other similar quicklimes generally have a high temperature rise which indicates a soft burned product capable of producing a finely-divided calcium hydroxide. Shaft kiln quicklimes generally have a low temperature rise indicating their inability of producing as finely divided calcium hydroxide as rotary kiln quicklime. Both types of dry calcium hydroxide may have the same percentage passing a 325 mesh sieve, which might indicate equal quality as far as fineness is concerned, but this is not true. The real difference in the products is the size of the particles or distribution of sizes smaller than 325 mesh. Two evaluations may be used to denote this difference. One of these is the settling rate of a ten per cent suspension to one-half volume in a 100 ml graduated cylinder. Calcium hydroxide containing particles of large diameter will settle at a faster rate than a calcium hydroxide containing particles of small diameter.

Another method of evaluation is the determination of the specific surface or the mean particle diameter. This may be determined with the Blaine air permeability apparatus.

The difference between shaft kiln and rotary kiln quicklimes is illustrated by the results of Table I.

TABLE I
Settling Time, Specific Surface and Mean Particle
Diameter of Calcium Hydroxides from Shaft Kiln and Rotary Kiln Quicklimes

Lime	Settling Time to 1/2 Volume Minutes	Specific Surface cm ² /g	Mean Diameter u
Shaft Kiln "A"	50	14,451	1.8
Shaft Kiln "B"	40	13,624	2.0
Rotary Kiln "A"	133	30,238	0.9
Rotary Kiln "B"	150	29,379	0.9

A great many chemical processes were established on calcium hydroxide produced from shaft kiln quicklime before the widespread production of rotary kiln quicklime. These industries may be able to use a hydrated lime produced from a rotary kiln quicklime, but most generally it means the investment in additional equipment or an alteration in the process to compensate for the differences in physical properties. A great many industries can use this finer product without disadvantage. Also, a great many industries can and do use a much finer calcium hydroxide than is obtainable commercially in a dry form from either shaft kiln or rotary kiln quicklimes. These industries must produce their calcium hydroxide from quicklime slaked in an excess of water.

2. Special Dry Hydrate

A study of the dry hydration of calcium oxide at temperatures greater than 212° F indicated that the diameter of the particles could be increased as denoted by a decrease in specific surface or an increase in mean particle diameter.

A decrease in specific surface or increase in mean particle diameter decreases the settling time of the dry product. This increase of particle diameter is proportional to the increase in temperature of hydration above 212° F. The increase in temperature of hydration is accomplished by regulating amount and rate of water addition to produce a high temperature that will maintain all the water as liquid and vapor, or vapor alone at atmospheric pressure until hydration is complete. This method of hydration can be used to reduce the settling time of dry calcium hydroxide to approximately one-third that of commercial dry rotary kiln calcium hydroxide produced by conventional methods and is comparable to calcium hydroxide produced from shaft kiln calcium hydroxide.

The reaction of calcium oxide in an excess of water, which we choose to call wet slaking, offers a great magnitude of variation of particle diameter control by a single method. Because the chemical industry uses this method exclusively in processing calcium oxide it offers great opportunity to standardize calcium hydroxide suspensions with constant physical properties.

B Wet Slaking

It is indeed interesting that the exothermic reaction of calcium oxide and water offers such control of particle diameter by slaking the calcium oxide in an excess of water. When a particle of soft burned calcium oxide is dropped in water, the lime immediately absorbs the water into the interstices left by the escaping carbon dioxide during the calcination process, and wets every part of the particle. Hydration begins immediately. When the lime is over-burned or when shaft kiln calcium oxide is used, the reaction rate is considerably slower. If the particle of calcium oxide is considered to be made up of many smaller particles, these very small particles will disintegrate during the hydration to produce even smaller particles of calcium hydroxide. The rate of reaction or the degree of hydration should then offer some means of controlling the size of the resulting calcium hydroxide particles. The process involving only sufficient water to produce a dry calcium hydroxide has been known as hydration, while the reaction utilizing an excess of water has been known as slaking. The two chemical reactions are identical as far as producing a calcium hydroxide is concerned, the only difference being that hydrating produces a dry product and slaking is spoken of as producing a suspension.

Realizing that the liberation of 27,500 Btu of heat per lb-mol of calcium oxide could have considerable influence on the development of the particle diameter of calcium hydroxide, the reactions were carried out not only with water at various temperatures from 4° C (39° F) to 90° C (194° F), but also at concentrations from 2.5 pounds of water per pound of calcium oxide to 25 pounds of water per pound of calcium oxide. This range in temperature would give us all practical values between the freezing and boiling points of water. The range of concentration would likewise be from the most concentrated suspension to a diluted suspension which would be feasible in any chemical process.

IV HEAT DISTRIBUTION CALCULATIONS

The liberation of a large amount of heat from the reaction between calcium oxide and water makes it desirable to study the effect of this heat on the hydrating mass. It is desirable to determine the distribution of heat in dry hydrating as well as wet slaking to better understand the possibilities of particle size control. The amount of heat developed and its distribution or dissipation controls the particle size and the particle size distribution of a calcium hydroxide and these calculations may be helpful in better understanding its effect.

A Dry Hydration

1 Conventional Dry Hydrates

Nearly every lime producer operates a hydrating plant for the production of a dry commercial calcium hydroxide. These plants are normally operated by the conventional process of adding sufficient water to convert the calcium oxide to calcium hydroxide at temperatures not exceeding 214° F (elevation of the boiling point of water by about 2° F by the presence of the solid calcium hydroxide).

Theoretical calculations for the use of 0.75 pound water per pound of calcium oxide, without heat loss from radiation, are shown in Table II. These calculations show that theoretically 94.3% of the water is used for hydrating and dissipating the heat, leaving 5.7% in the finished product. This amount of water constitutes 3.14% of the finished product.

This calculation is not exactly true, because no corrections were made for radiation losses. Neither were allowances made for the amount of recovered water from escaping steam normally captured by one of the sprays in the system. The efficiency of the hydrating machine or the amount of heat losses will determine whether this amount of water is sufficient to completely convert the calcium oxide to calcium hydroxide. Practical operation of the process in a hydrator with low radiation losses produces a finished product with 0.5% or less free moisture.

2 Special Dry Hydration

It has been found that the development of higher temperatures in the production of a dry calcium hydroxide has a desirable effect on increasing the particle size. Calculations illustrating the temperatures possible by this process have been made.

Theoretical calculations for the operation of such a process above 212° F are shown in Table III. When 0.40 pound water per pound calcium oxide

(Cont - pg. 16)

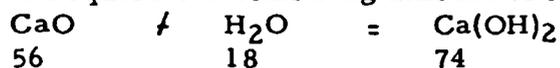
TABLE II

Basis: Normal Hydration

56 lbs. CaO (1 lb-mol)
42 lbs. H₂O (0.75 lbs. H₂O per lb. CaO)

42 lbs. H₂O added to CaO at one time.

56 lbs. CaO will require the following amount of H₂O for theoretical hydration:



Therefore 18 lbs. of water will be used for converting CaO to Ca(OH)₂
Excess H₂O will be 42 - 18 = 24 lbs.

Total heat evolved in combining 56 lbs. CaO / 18 lbs. H₂O = 27,500 Btu

Amount of heat required to raise the temperature of 24 lbs. H₂O from
70° F to 214° F = (24) (144) = 3452 Btu

Amount of heat required to raise the temperature of 74 lbs. Ca(OH)₂ from
70° F to 214° F = (74) (0.29) (144) = 3089 Btu

Therefore, the heat required to heat both Ca(OH)₂ and H₂O from
70° F to 212° F = 3452 / 3089 = 6541 Btu

Remaining Btu's available for heating 24 lbs. excess H₂O above 214° F is
27,500 Btu - 6541 Btu = 20,959 Btu

Quantity of water which can be evaporated at 212° F with this quantity of
heat will be:

$$\frac{20,959}{970} = 21.6 \text{ lbs.}$$

Water as liquid at 212° F remaining in 74 lbs. Ca(OH)₂ will be
24.0 - 21.6 = 2.4 lbs. or

The composition of the finished product will be, therefore 74.0 lbs.

Ca(OH)₂ / 2.3 lbs. excess water or a total weight of 76.3 lbs.

Water	2.4 lbs.	3.14%
Ca(OH) ₂	74.0 lbs.	96.86%
<hr/>		<hr/>
Total	76.5 lbs.	100.00%

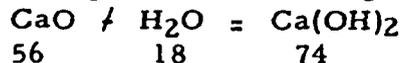
TABLE III

Basis: Special Hydration for size control

56 lbs. (1 lb-mol)
22.4 lbs. (0.40 lbs. H₂O per lb. CaO)

22.4 lbs. H₂O added under controlled conditions

56 lbs. CaO will require the following amount of H₂O for theoretical hydration



Therefore, 18 lbs. of H₂O will be used in converting CaO to Ca(OH)₂
Excess H₂O will be 22.4 - 18 = 4.4 lbs. H₂O per 56 lbs. CaO

Total heat evolved in combining 56 lbs. CaO + 18 lbs. H₂O = 27,500 Btu

Amount of heat required to raise the temperature of 4.4 lbs. H₂O from
70° F to 212° F = (4.4) (142) = 625 Btu

Amount of heat required to raise the temperature of 74 lbs. Ca(OH)₂ from
70° F to 212° F = (74) (0.29) (142) = 3057 Btu

Therefore, the heat required to heat both Ca(OH)₂ and H₂O from
70° F to 212° F = 625 Btu + 3057 Btu = 3682 Btu

Remaining Btu's available for heating 4.4 lbs. excess H₂O above 212° F is
27,500 Btu - 3682 Btu = 23,818 Btu

Quantity of water which can be evaporated at 212° F with this quantity of
heat will be:

$$\frac{23,818}{970} = 24.6 \text{ lbs.}$$

Since there is less water than this in the mass, a different method calculation
must be made. The amount of heat necessary to evaporate 4.4 lbs. of H₂O
at 212° F is:

$$(4.4) (970) = 4268 \text{ Btu}$$

Excess heat still available is 23,818 - 4268 = 19,550 Btu

Heat required for 74 lbs. Ca(OH)₂ from 212° F to 575° F will be
(74) (0.29) (363) = 7790 Btu

Heat available for heating water vapor only = 19,550 - 7790 = 11,760
Temperature attainable = (4.4) (0.48) (x - 212) = 15,516

$$\text{or } x = \frac{12,207}{2.11} = 578^\circ \text{ F}$$

is used and added at such a rate that evaporation is maintained throughout the process to provide vapor for hydration, it is shown that theoretically temperatures of 578° F can be maintained.

Greater quantities of water, to a maximum of 0.75 pound water per pound calcium oxide, will decrease the final temperatures to that for conventional hydration as shown in Table II. A decrease in final temperature results in a decrease in mean particle diameter or an increase in specific surface. An increase in specific surface is accompanied by an increase in settling time of the calcium hydroxide.

B WET SLAKING

The theoretical temperatures expected from the reaction of calcium oxide and water were calculated for water temperatures from 4°C (39° F) to 90° C (194° F) and for water-to-calcium oxide ratios from 2.5 pounds to 25 pounds. The calculations are based upon a constant weight to give 0.503 pound pure calcium oxide. Water ratios of 2.5, 7.5, 10.5, 13.5, 18.5 and 25 corresponding to excess weight of water of 1.16, 3.81, 5.39, 6.98, 9.36 and 13.06 pounds respectively were used.

Calcium oxide in the amount of 0.503 pound will produce 0.665 pound calcium hydroxide. The theoretical heat evolved by 0.503 pound calcium oxide during hydration is 246.9 Btu.

The amount of heat required to raise the temperature of water to any temperature up to and including 212° F (boiling), where

- H = the heat in Btu
- W = the weight of water
- h = the heat capacity of water = 1
- T₁ = the initial temperature of the water, and
- T₂ = the final temperature of water

is calculated from the equation

$$H = (W) (h) (T_2 - T_1) \text{ or } (W) (T_2 - T_1) \quad (2)$$

The amount of heat required to raise the temperature of calcium hydroxide where

- H' = the heat in Btu
- W' = the weight of calcium hydroxide
- h' = the heat capacity of calcium hydroxide = 0.29
- T'₁ = the initial temperature
- T'₂ = the final temperature

is calculated from the equation

$$H' = (W')(h')(T'_2 - T'_1) \text{ or } (W')(0.29)(T'_2 - T'_1) \quad (3)$$

When a constant weight of 0.503 pound calcium oxide is used with a value for H of 246.9 Btu and a weight for calcium hydroxide of 0.665 pound the equations become

$$246.9 = (W)(T_2 - T_1) \quad (4)$$

and

$$H = (0.665)(0.29)(T'_2 - T'_1) = (0.193)(T'_2 - T'_1) \quad (5)$$

respectively.

The total heat derived from the hydration reaction is the distribution of the evolved heat from the calcium oxide between the water and the calcium hydroxide to the same temperature. It is the sum of the heat required to raise the temperature of the water and the heat required to raise the temperature of the calcium hydroxide to the same temperature.

The combined equation then becomes Equations (4) + (5) or

$$H = W(T_2 - T_1) + W'h'(T'_2 - T'_1) \quad (6)$$

or

$$H = (W)(T_2 - T_1) + 0.193(T'_2 - T'_1) \quad (7)$$

The final temperature of hydration can be calculated from this equation by solving for T_2 since $H = 246.9$ Btu. The equation then becomes

$$T_2 = \frac{H + (0.193 + W) T_1}{0.193 + W} \quad (8)$$

When it becomes desirable to calculate the temperature necessary to start a reaction with a given weight of calcium oxide to theoretically result in a final temperature of 212° F the equation becomes

$$T_1 = \frac{(0.193 + W) T_2 - 246.9}{0.193 + W} \quad (9)$$

The theoretical final temperatures expected from the same weight of pure calcium oxide (0.503 lb.) with various ratios of water at several temperatures as calculated by equation (7) are shown in Table IV.

TABLE IV

(following page)

TABLE IV

Theoretical Slaking Temperature ($^{\circ}\text{F}$) of calcium oxide with water at various temperatures and proportions.

Ratio $\text{H}_2\text{O}/\text{CaO}$	Excess H_2O lbs.	Temperatures of Slaking Water					
		4°C 39°F	10°C 50°F	20°C 68°F	40°C 104°F	60°C 140°F	90°C 194°F
2.5	1.16	221.4	232.5	250.3	286.3	322.5	376.4
7.5	3.81	100.7	111.8	129.7	165.7	201.7	255.7
10.5	5.39	83.2	94.2	112.2	148.2	184.2	238.2
13.5	6.98	73.4	84.4	102.4	138.4	174.4	228.3
18.0	9.36	64.8	75.9	93.9	129.8	165.7	210.7
25.0	13.06	57.6	68.6	86.6	122.6	158.6	212.6

Temperatures in excess of 212°F are shown above and to the right of a dotted line, indicating that insufficient water is present to absorb the liberated heat and therefore part of the water will be evaporated during the slaking cycle. Temperatures of calcium hydroxide suspensions less than boiling (212°F) can be expected from the reacting between calcium oxide and water for ratios greater than 7.5 and for all temperatures from 39°F (4°C) to 140°F (60°C).

The initial temperature of water for the reaction of all ratios of water to calcium oxide to give a final temperature of 212°F were calculated by equation (8). These initial temperatures are shown in Table V.

TABLE V

THEORETICAL INITIAL TEMPERATURE (T_1) ($^{\circ}\text{F}$) OF SLAKING WATER TO GIVE A FINAL SLAKING TEMPERATURE (T_2) OF 212°F .

Ratio $\text{H}_2\text{O}/\text{CaO}$	Excess Water Lbs.	T_1		T_1 corrected for radiation loss	
		$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$
2.5	1.16	29.6	-1.4	54.6	12.6
7.5	3.81	150.3	65.6	166.8	74.9
10.5	5.39	167.7	75.4	180.1	82.3
13.5	6.98	177.5	80.8	185.8	85.4
18.0	9.36	186.1	85.6	196.5	91.4
25.0	13.06	193.4	89.6	205.0	96.0

All of these calculations have been made to illustrate the wide temperature variations expected in using a variation of ratios and temperatures of water to effect the development of particle diameters of calcium hydroxide in aqueous suspension and to compare the theoretical values with the actual values. It should be emphasized that the degree of rotary kiln calcination of a limestone may affect the rate of slaking and therefore all calcium oxides may not reach these expected temperatures. Only soft-burned calcium oxide will check the values.

V METHOD OF WET SLAKING

A very reactive rotary kiln pebble calcium oxide was used for this study. The reactivity was measured by testing the temperature of 180 grams of the pebble calcium oxide in 900 ml of water at 24° C in an insulated stainless steel beaker. The temperature rise in 30 seconds was 33° C. The quality of the calcium oxide was determined by the sugar method for calcium oxide. It was found to contain 95% calcium oxide.

A Procedure

The procedure for preparing suspensions of calcium hydroxide employed 240 g of pebble calcium oxide for each sample. The amount of water for the preparation of the suspensions ranged from a ratio (R) of 2.5 to 25 times the weight of calcium oxide. A tabulation of the weight of calcium oxide and the volume of water are shown in Table VI.

TABLE VI

Weight of CaO and Volume of H₂O used for
Preparing Ca(OH)₂ Suspensions

R	Rotary Kiln Pebble CaO g	Total Water ml	Excess Water	
			g	lbs.
2.5	240	600	527	1.16
7.5	240	1800	1727	3.81
10.5	240	2500	2447	5.39
13.5	240	3240	3167	6.98
18.0	240	4320	4247	9.36
25.0	240	6000	5927	13.06

The water for each slaking test was heated to the required temperature. The weighed amount of rotary kiln pebble calcium oxide was added to the water at one time. The mixture was mechanically stirred and the reaction temperature measured with a thermometer calibrated to 0.1°C. Agitation was continued until the temperature reached a maximum and began to recede.

The proper agitation of a mixture of calcium oxide and water during the hydration cycle is of the utmost importance. Agitation must be provided to prevent local overheating of the calcium oxide, especially in large quantities of water, and to assure that each particle of lime is supplied constantly with a fresh supply of necessary water to carry out the entire hydration reaction. The most satisfactory method of agitation was found to be supplied by a stirrer having two arms perpendicular to each other and of sufficient length to extend almost to the periphery of the reaction vessel. The agitator speed was controlled during the hydration cycle to provide maximum agitation without overflowing the vessel.

The suspensions of very high solids concentration were very difficult to agitate to a homogeneous mass. The evaporation of water was so rapid that it was difficult to prevent local drying before the temperature decreased below the boiling point. This condition may introduce errors of accurate temperature determination of the slaking reaction.

B Method of Testing

1. Specific Surface

A sample of each suspension was taken immediately after hydration was complete for a specific surface determination. Approximately 100 - 250 ml of the suspension were filtered on a 3-inch Buechner funnel under vacuum, washed with five portions of alcohol to remove the water and then washed with five portions of ether to remove most of the alcohol. The evacuated sample was then dried under infra-red heat until all of the ether and most of the alcohol had been evaporated. The sample was finally dried for approximately 30 minutes in an oven at 105 to 110°C.

A weight of 1.30 g of dried powder was used for determining the specific surface of each sample.

2. Settling Time

Each suspension was then stored in a 1/2 gallon sealed mason jar to allow cooling to room temperature. Then each well mixed suspension was analyzed by the sugar method to determine the concentration of calcium hydroxide in grams per liter. The suspension was then diluted with water or decanted of clear supernatant liquid to give 100 grams per liter of calcium hydroxide and rechecked by the sugar method. This concentration is equivalent to 10 grams of dry calcium hydroxide in 100 ml of suspension for the settling time test. Settling rate was then determined on 100 ml each of suspension by noting the time-rate required to settle to 50 ml (1/2 volume) for those samples which would settle to this point, or to determine the minimum volume each suspension of calcium hydroxide would assume when

no settling value could be obtained. The latter condition existed for those samples having a high specific surface, indicating a bulkiness for the extremely fine particles.

3. Viscosity

It is known that the viscosity of calcium hydroxide suspensions can be increased by dispersing the particles more completely in the liquid vehicle. It is also known that the increase in viscosity in a given suspension is accompanied by an increase in specific surface when there is no change in the water ratio of the suspension. The increase in specific surface increases the settling time of the particles in the suspension. The degree of dispersion of particles during wet slaking is proportional to the degree of calcination of the limestone and the temperature and ratio of the slaking water.

It is not the intention to go into details of the viscosity of calcium hydroxide suspensions in this report, but to briefly touch on the subject to show that some relation exists between the quality of the calcium oxide, the method of slaking and the characteristics of the resulting calcium hydroxide.

All types of calcium oxide will not produce aqueous suspensions of calcium hydroxide of equal viscosity at the same concentration by the same procedure of slaking. For example, one type of calcium oxide slaked in six parts water at 20° C (68° F) and stirred for five minutes produces a calcium hydroxide suspension with a viscosity of 46 centipoises while another type of calcium oxide slaked under exactly the same conditions of stirring and water temperature and ratio produced an aqueous suspension of calcium hydroxide with a viscosity of 273 centipoises. These same calcium oxides slaked in exactly the same manner but using water at a temperature of 60° C (140° F) produced suspensions of calcium hydroxide having viscosities of 716 centipoises and 395 centipoises respectively. Further agitation of these suspensions produced some surprising results. The suspensions produced with slaking water at 20° C and stirred for twenty-five minutes after slaking was complete yielded viscosities of 200 centipoises and 288 centipoises respectively. The suspensions produced with slaking water at 60° C and stirred for twenty-five minutes after slaking was complete had viscosities of 3875 centipoises and 390 centipoises respectively.

Far too little study has been made on the viscosity of calcium hydroxide suspensions from various types of calcium oxide to understand the mechanics of viscosity control. The viscosity of suspensions produced for this report was determined for various concentrations. The determinations were made with a standard Brookfield viscometer.

VI RESULTS

A Slaking Temperatures and Slaking Time

The slaking temperatures of samples for all concentrations and initial water temperatures are shown in Table VII.

TABLE VII

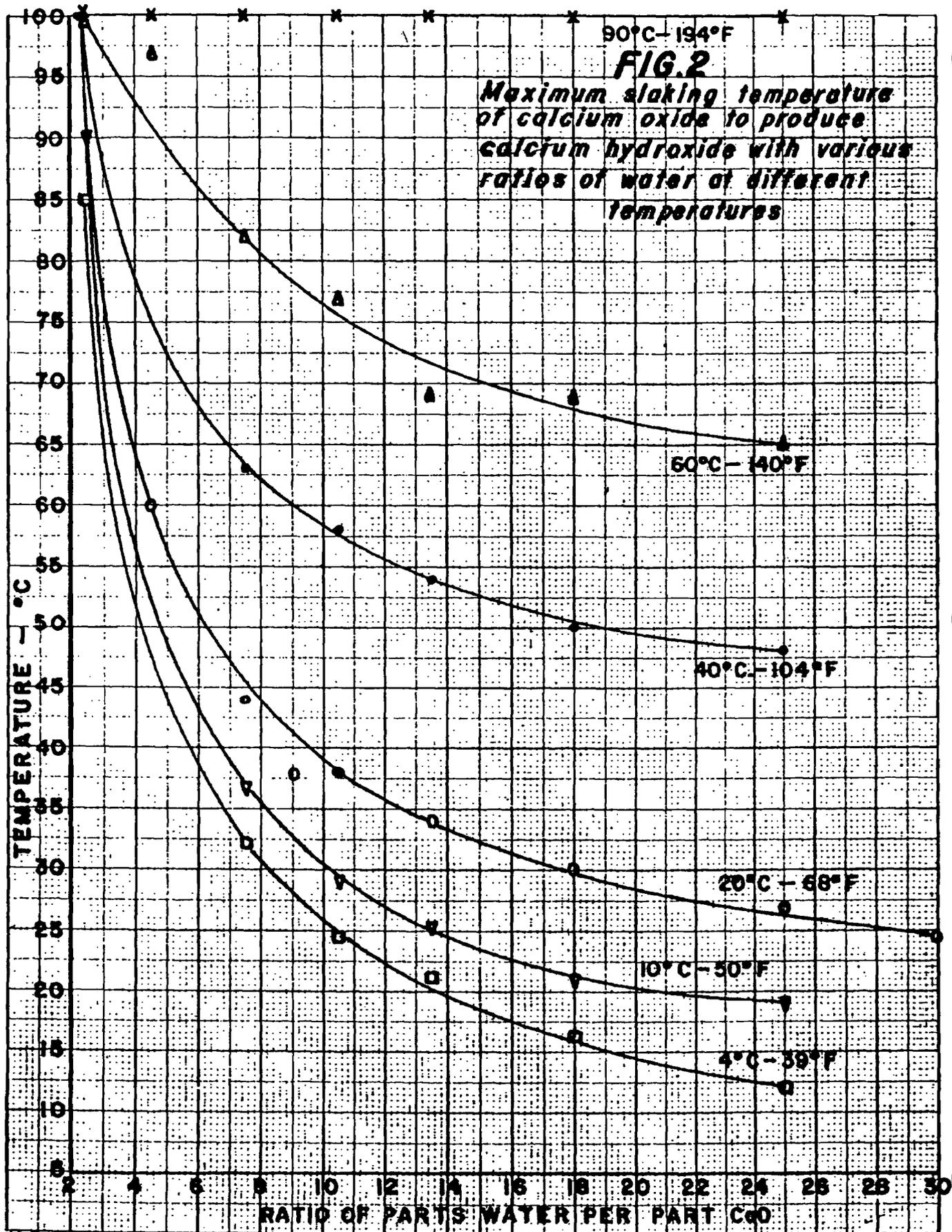
Maximum Slaking Temperatures of CaO with Various Amounts of Water at Various Temperatures

R	<u>Initial Water Temperature</u>											
	4		10		20		40		60		90	
	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$
2.5	85	185	90	194	100	212	100	212	100	212	100	212
7.5	32.2	90	36.5	98.7	43.6	110.5	63	145.4	82	179.6	100	212
10.5	24.6	76.3	29	84.2	38	100.4	58	136.4	77	170.6	100	212
13.5	21.2	70.2	25.5	77.9	34.8	94.7	54	129.2	69	156.2	100	212
18.0	16.0	60.8	21.6	70.9	30.6	87.1	50	122.0	69	156.2	100	212
25.0	12.2	52	19.0	66.2	27.8	82.0	48	118.4	65	149.0	100	212

These values are also shown graphically in Figure 2.

Temperatures less than 100°C (212°F) are shown to the left and below a dotted line.

A comparison of these actual slaking temperatures with the theoretical expected temperatures indicated quite a variation. The percentage differences between these two values, based upon the theoretical, are shown in Table VII-A. No values are shown for tests with R at 2.5 or a temperature of 194°F .



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TABLE VII-A

Percentage Difference between Theoretical and Actual Slaking
Temperature

<u>R</u>	<u>Initial Water Temperature °F</u>				
	<u>39</u>	<u>50</u>	<u>68</u>	<u>104</u>	<u>140</u>
7.5	10.6	11.7	14.8	12.3	11.0
10.5	8.3	10.6	10.5	7.97	7.4
13.5	5.5	7.7	7.5	6.6	4.7
18.0	6.2	6.6	7.2	6.0	5.7
25.0	9.7	3.5	5.3	3.4	6.0

No correction was made in the theoretical calculations for heat loss in the steel container or for the radiation loss. A correction for heat loss in the steel slaking vessel would have been constant to give a uniform lower percentage difference between the theoretical and actual results. Radiation losses would be expected to be greatest at the higher temperatures which would result in a greater temperature difference. This, however, is not exactly true. Greatest losses were found to be at the lower values of R. The initial temperature of the slaking water appears to have little influence in increasing these losses. For example, at initial temperature of 60°C (140°F) the final slaking temperature was approximately 150°F or greater with percentage difference between theoretical and actual less than many other tests at lower initial water temperature. There is a general trend for lower percentage differences between theoretical and actual slaking temperatures with an increase in the value of R.

All rotary kiln calcium oxides will not produce slaking temperatures corresponding exactly to these values. The activity or slaking rate of the calcium oxide (V-1, p. 19) and the viscosity of the calcium hydroxide suspension will affect the final slaking temperature. Regardless of the activity of the calcium oxide the slaking temperature will be proportionate to the values shown as changes in R and water temperature are made. These data indicate anticipated temperatures to be expected for changes in R and T₁.

The time for the reaction between calcium oxide and water to be completed is dependent upon both the solids concentration and the initial temperature of the water. An increase in the ratio of water at a given temperature increases the slaking time, but an increase in the initial water temperature at a given concentration decreases the slaking time.

The approximate slaking time for each sample prepared is shown in Table VIII. The values give the slaking time to the nearest minute for the temperature to reach a maximum.

TABLE VIII

Slaking Time (Minutes) of CaO with Various Amounts of Water at Various Temperatures

		<u>Initial Water Temperature</u>					
		10	20	40	60	90	
<u>°C</u>	<u>R</u>	<u>50</u>	<u>68</u>	<u>104</u>	<u>140</u>	<u>194</u>	
4	2.5	3	6	1	2	1	
8	7.5	16	7	3	2	1	
18	10.5	20	7	4	2	1	
13	13.5	23	8	4	2	1	
14	18.0	20	7	4	2	1	
18	25.0	12	8	4	2	1	

These values are shown graphically in Figure 3.

B Settling Time

The settling rate of each suspension, adjusted to 100 gpl Ca(OH)_2 , prepared at all concentrations and at temperatures of 4°, 10°, 20°, 40°, 60° and 90°C are shown in Tables IX, X, XI, XII, XIII and XIV respectively. The data is also shown graphically in Figures 4, 5, 6, 7, 8 and 9. A summary of the settling time to one-half volume (50 ml) for each sample is shown in Table XV and graphically in Figure 10. The volume occupied by the settled calcium hydroxide after 24 hours for each suspension is shown in Table XVI and shown graphically in Figure 11.

The settling time of a series of calcium hydroxide suspensions prepared with water of the same initial starting temperature increases as the ratio of water decreases for final temperatures less than 212°F. For example, using water at 4°C (39°F), the settling time is 80 minutes when the ratio is 25 pounds of water per pound of CaO and 480 minutes when the ratio of water has been decreased to 7.5 pounds water per pound CaO. Also, using water with an initial temperature of 60°C (140°F) the settling time is 835 minutes when the ratio is 25 pounds water per pound calcium oxide and 1800 minutes when the ratio is decreased to 7.5 pounds water per pound calcium oxide.

FIG. 3

Approximate Slaking Time (in minutes) required to produce Calcium Hydroxide from Calcium Oxide and various ratios of water at 4°C, 10°C, 20°C, 40°C, 60°C & 90°C.

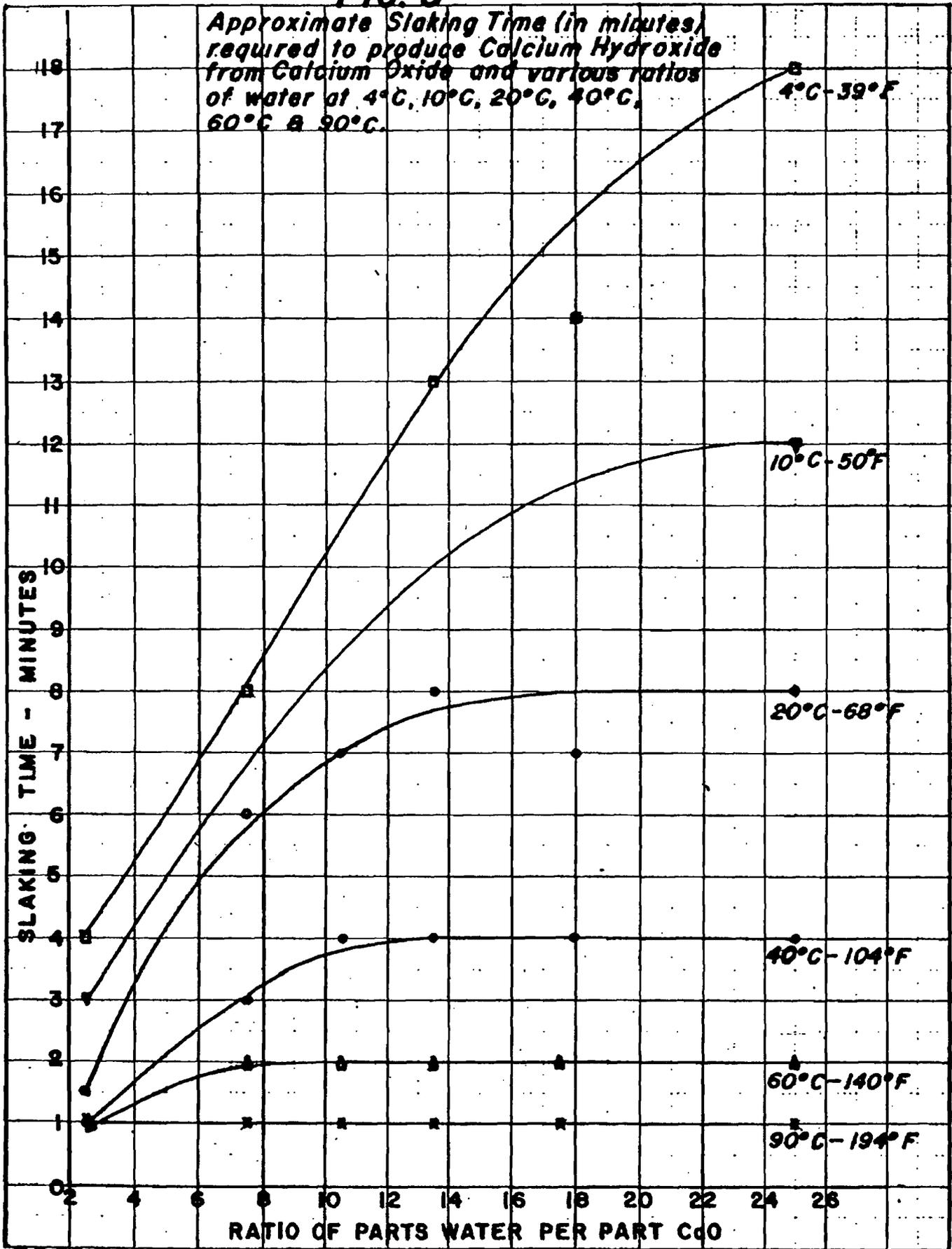


TABLE IX

SETTLING RATES OF HYDRATES

Temp. °C	4	4	4	4	4	4
°F	39	39	39	39	39	39
R	2.5	7.5	10.5	13.5	18	25
Min. (hr.)						
0	0	0	0	0	0	0
5	1	1.5	1.5	1.5	3	1.5
10	2	2.5	4.0	5	5.5	7.5
15	2.5	4.5	7.0	9	8.5	14.5
20	3	6.5	10.5	13.0	11	22.5
25	3.5	9.5	15.0	18.5	14	32.0
30	4	11.5	18.0	22.5	16	37.0
35	5	13.5	21.5	26.5	18.5	40.0
40	6	16.5	25.5	32.5	21	42.0
45	7	18.5	30.5	37.0	23.5	43.0
50	9	21.0	34.0	39.0	26	44.5
55	11	24.5	36.0	41.0	28.5	45.5
60 (1)	13	28.5	37.0	42.0	31	46.5
70	15	31.5	39.0	44.0	37.5	48.5
80	-	33.5	40.5	45.0	-	50.0
90	18	35.0	42.0	46.5	46.5	51.0
100	-	36	43.0	47.5	-	52.0
110	20.0	37	43.5	48.5	49.0	53
120 (2)	20.5	38	44.5	49.0	50.0	54
135	21.5	39	45.5	50.0	51	55
150	22.5	40	46.5	51.0	52	56
165	23.5	41	47.5	52	53	57
180 (3)	24.0	41.75	48.25	52.75	54	58
195	25.0	42.5	49.0	53.5	55	58.5
210	-	43.25	49.75	54.0	-	59 +
225	27.0	43.75	50.00	54.75	57	59.75
240 (4)	-	44.25	50.5	55 +	-	60 +
270	28.0	45.5	52	56.5	57.5	61.5
300 (5)	29.0	46 +	52.75	57	58.5	62
330	30	47.0	53.5	58	59	62.5
360 (6)	31	48.0	54.25	58.75	59.5	63
390	31.5	48.5	55.0	59.25	59.75	63.5
420 (7)	32.25	49.25	55.5	59.75	60	64.0
480 (8)	33.5	50.0	56.0	60 +	60	64.0
540	-	50.5	56.5	60.5	-	64.5
1440 (24)	44	57	61	63.4	61	66

TABLE X
SETTLING RATES OF HYDRATES

Temp. °C	10	10	10	10	10	10
° F	50	50	50	50	50	50
R	2.5	7.5	10.5	13.5	18	25
Min. (hr)						
0	0	0	0	0	0	0
5	0.5	1	1	0.5	1	1.5
10	1.5	3	3.5	2.5	3	8.5
15	2.5	4.5	5.5	5.0	6	15.0
20	4	7.0	8.5	8.0	10.5	21.5
25	6	10.0	12.0	12.0	15.5	30.0
30	8	12.0	14.0	14.5	20	37.0
35	9	14.0	17.0	17.5	25.5	41.5
40	10	16.0	19.5	20.5	32	43.5
45	11	19.0	23.0	24.0	37	45.0
50	12.5	22.0	26.0	27.0	39	46.0
55	13.5	25.0	30.0	32.0	40.5	47.5
60 (1)	14.25	29.5	34.5	36.5	41.5	48.5
70	15.5	33.0	38.0	40.0	43.75	50.0
80	16.5	35.0	40.0	42.0	45	51.0
90	17.5	36.5	41.5	44.0	46.5	52.5
100	-	37.5	43.0	45.0	-	53.0
110	19.5	38.5	43.5	46.0	48.5	54.0
120 (2)	20	39.5	44.5	47.0	49.5	55.0
135	21	40.5	45.5	48.0	50.75	56.0
150	22	41.5	46.5	49.0	51.75	56.75
165	23	42.5	47.5	50.0	52.75	57.5
180 (3)	23.75	43.25	48.5	51.0	53.5	58.25
195	24.5	44.0	49.0	51.75	54.25	59
210	25.7	45.0	50.0	52.50	55	59.5
225	-	45.25	50.5	53.0	-	60.0
240 (4)	26.5	46.0	51.0	53.75	56	60.5
270	-	47.25	52.5	55	-	61.5
300 (5)	28.5	48.0	53.25	56	-	62
330	-	49.0	54.25	57	-	62.75
360 (6)	-	49.75	55.0	57.5	-	63.25
390	-	50.5	56.0	58.5	-	63.75
420 (7)	-	51.7	56.5	59.0	-	64.0
480 (8)	-	51.75	57.0	59.5	-	64.25
540	-	52.5	57.75	60.0	-	64.5
1440 (24)	43	58	61.5	63	60	66

TABLE XI
SETTLING RATES OF HYDRATES

Temp. ° C	20	20	20	20	20	20
° F	68	68	68	68	68	68
R	2.5	7.5	10.5	13.5	18	25
Min. (hr)						
0	0	0	0	0	0	0
5	0.5	1.0	1.0	2.0	2.0	2.0
10	1.0	2.5	2.5	4.5	4.5	6.0
15	1.5	4.5	4.0	7.0	8.0	10.5
20	2.0	7.0	6.0	10.0	12.0	15.0
25	2.75	9.0	8.0	13.0	15.5	19.5
30	3.25	11.0	10.0	15.5	19.0	24.0
35	3.75	13.5	12.25	18.75	23.0	28.5
40	4.25	15.5	14.5	21.75	26.75	34.0
45	4.75	17.5	16.0	24.0	30.0	39
50	5.0	20.0	18.5	27.5	34.5	42.5
55	5.5	23.0	21.25	31.0	39.5	44.5
60 (1)	6.0	25.75	24.5	35.0	42.5	45.75
70	6.75	31.5	31.0	42.0	44.75	47.5
80	7.5	37.5	34.5	43.0	46.5	49.0
90	8.0	39.5	36.5	45.5	47.75	50.0
100	8.75	41.0	38.0	46.75	49.0	51.5
110	9.0	42.0	39.0	47.5	50.0	52
120 (2)	10.0	43.0	40.0	48.5	50.5	53.0
135	10.5	44.5	41.0	49.75	51.75	54.0
150	11.25	45.5	42.0	50.75	52.5	55.0
165	12.00	46.5	43.0	51.75	53.25	56.0
180 (3)	12.75	47.5	44.0	52.5	54.0	57.0
195	13.5	48.0	45.0	53.5	55.0	57.5
210	13.75	48.5	45.0	54.0	55.5	58.0
225	14.5	49.5	46.0	54.5	56.0	58.5
240 (4)	15.0	49.75	46.5	55.0	56.5	59.0
270	16.0	51.0	47.5	56.0	57.75	60.0
300 (5)	17.0	52.0	48.75	57.0	58.75	61.0
330	18.0	53.0	49.75	58.5	59.75	62.0
360 (6)	18.75	54.0	50.5	59.0	60.0	62.5
390	19.5	54.75	51.0	59.5	61.0	63.0
420 (7)	20.5	55.5	52.0	60.25	61.5	63.25
480 (8)	22.0	56.5	53.0	61.0	62.50	64.0
540	23.0	57.5	54.0	62.0	63.0	64.5
600 (10)	24.5	58.5	55.0	62.5	63.5	65.0
660	26.0	59.0	55.75	63.0	64.0	65.0
960 (16)	31.75	60.75	58.5	64.0	65.0	65.75
1200 (20)	34.25	61.25	59.0	64.25	65.0	65.75
1440 (24)	37	61.5	59.0	64.25	65.0	66.0

TABLE XII

SETTLING RATES OF HYDRATES

Temp. °C	40	40	40	40	40	40
	104	104	104	104	104	104
R	2.5	7.5	10.5	13.5	18	25
Min. (hr)						
0	0	0	0	0	0	0
5	5	1.0	1.0	1.0	2.0	2.0
10	1.0	2.5	1.5	1.5	2.0	3.0
15	2.0	2.5	3.0	3.0	4.0	5.5
20	2.5	4.0	4.0	5.0	6.0	7.75
25	3.0	4.75	5.25	6.5	7.75	10.0
30	4.0	6.0	7.0	8.25	9.75	12.0
35	4.75	7.0	8.0	10.0	11.5	14.5
40	6.0	8.5	9.75	12.0	13.5	17.0
45	7.0	10.0	11.0	13.5	15.5	19.0
50	8.5	11.0	12.25	15.5	17.5	21.25
55	10.0	12.5	14.0	17.5	20.0	23.0
60 (1)	12.0	14.0	15.5	20.0	22.0	27.0
70	15.0	17.0	18.5	24.0	27.0	33.0
80	16.0	20.0	22.0	28.5	32.0	39.5
90	17.25	23.5	26.0	34.0	38.0	42.0
100	18.5	28.0	30.5	37.75	40.25	43.50
110	19.0	31.5	34.5	39.0	41.5	44.5
120 (2)	20.0	33.0	36.5	40.0	42.5	45.5
135	21.0	35.0	38.0	41.75	44.0	47.0
150	21.75	36.0	39.75	43.0	45.0	48.0
165	22.75	37.0	41.0	44.0	46.0	49.0
180 (3)	23.5	38.0	42.0	45.0	47.0	50.0
195	24.0	39.0	42.5	45.5	47.75	50.5
210	24.5	39.5	43.0	46.0	48.0	51.0
225	25.0	40.0	44.0	47.0	49.0	51.5
240 (4)	25.75	40.75	44.5	47.5	49.5	52.5
270	27.0	42.0	45.5	48.5	50.5	53.5
300 (5)	28.0	43.0	46.75	49.75	52.0	54.5
330	29.0	44.0	48.0	50.5	53.0	55.5
360 (6)	29.5	44.5	48.5	51.5	53.75	56.25
390	30.0	45.5	49.5	52.0	54.5	57.0
420 (7)	31.0	46.0	50.0	53.0	55.0	57.5
480 (8)	32.25	47.25	51.5	54.25	56.5	58.75
540	33.5	48.5	52.5	55.25	57.5	59.5
600 (10)	34.5	49.5	53.5	56.0	58.5	60.5
660	35.5	50.5	55.0	57.0	59.0	60.75
960 (16)	40.0	54.0	58.0	59.5	61.0	62.25
1200 (20)	41.0	54.5	58.25	60.0	61.0	62.5
1320 (22)	42.0	54.75	58.5	60.0	61.0	62.5
1440 (24)	43.0	55.0	58.75	60.0	61.0	62.5

TABLE XIII

SETTLING RATES OF HYDRATES

Temp. °C	60	60	60	60	60	60
°F	140	140	140	140	140	140
R	2.5	7.5	10.5	13.5	18	25
Min. (hr)						
0	0	0	0	0	0	0
5	1	1	1	1	1	2
10	2	2	2	2	2	2.5
15	2.5	2.5	2.1	2.1	2.5	4.0
20	3.0	3.2	3.2	3.2	3.5	5.0
25	4.0	4.0	4.0	4.3	4.5	6.0
30	5.0	5.1	5.0	5.5	5.5	7.5
-	-	-	-	-	-	-
60 (1)	10.1	10.5	10.0	12.0	12.0	16.0
90	14	18.0	18.0	21.0	21.0	27.1
105	15	22.8	20.8	26.0	27.0	29.0
120 (2)	16	26.0	26.0	30	29.2	31
135	17	27.8	27.0	32	31.0	32.5
150	17.5	29.0	29.8	33	32.0	33.5
240 (4)	21	34	34.8	38	38	38.5
300 (5)	22.8	36	36.9	40	39.0	40.5
330	23.5	37	37.8	41	40.0	41.7
360 (6)	24.0	37.9	38.8	41.9	40.9	42.5
370	25.0	38.5	39.1	42.5	41.4	43.2
420 (7)	25.6	39.0	40.0	43.0	42.0	44.0
480 (8)	26.9	40.2	41.0	44.1	43.1	45.1
600 (10)	29.0	42.3	43.1	46.4	45.2	47.2
660 (11)	29.9	43.1	44.0	47.3	46.1	48.1
720 (12)	30.6	44.0	45.0	48.0	47.0	49.0
780 (13)	31.6	44.9	45.9	48.9	48.0	49.8
840 (14)	32.1	45.3	46.3	49.6	48.4	50.1
900 (15)	33.0	46.0	47.0	50.0	49.0	50.9
960 (16)	33.8	46.6	47.7	50.7	49.6	51.2
1230	36.3	48.3	49.2	51.9	51.1	52.9
1380 (23)	37.6	49.0	50.0	52.5	51.5	53.2
1440 (24)	38.0	49.2	50.0	52.5	51.7	53.5

TABLE XIV

SETTLING RATES OF HYDRATES

Temp. °C	90	90	90	90	90
° F	194	194	194	194	194
R	4.5	7.5	10.5	13.5	18.0
Min (hr)					
0	0	0	0	0	0
5	1.0	1.0	1.0	0.5	0.5
10	1.0	1.0	1.0	0.5	1.0
15	1.8	2.0	2.0	1.0	1.4
20	2.6	2.6	3.0	2.0	2.1
25	3.4	4.0	3.8	2.4	3.1
30	4.5	5.0	4.9	3.5	4.0
35	5.0	5.8	5.6	4.2	4.8
40	6.0	7.0	6.8	5.0	5.2
45	7.1	8.0	7.5	6.0	6.0
50	8.0	9.0	8.0	6.6	7.2
55	9.0	10.0	9.0	7.2	7.9
60 (1)	10.0	10.9	10.0	8.2	9.2
70	11.1	12.8	12.8	10.0	11.8
80	13.0	15.1	13.8	11.9	14.9
100	17.5	20.8	17.8	15.8	22.0
110	20	24.1	20.0	18.1	24.0
120 (2)	23	27.2	22.9	21.1	25.1
150	29.6	30.4	31.0	29.9	28.1
165	31	31.6	32.1	31.2	29.1
180 (3)	32	32.8	33.8	32.8	30.0
210	33.8	34.1	35.0	34.3	32.0
240 (4)	34.1	35.8	36.8	36.0	33.2
300 (5)	37.4	37.7	38.8	38.1	35.3
330	38.1	38.5	39.8	39.1	36.6
360 (6)	39.1	39.1	40.5	40.0	37.1
390	40.0	40.0	41.1	40.9	38.0
420 (7)	40.6	40.6	41.9	41.7	38.9
480 (8)	42.0	41.9	43.1	43.0	39.9
540 (9)	43.0	43.0	44.2	44.0	41.1
660 (11)	44.8	44.8	46.2	46.0	43.0
780 (13)	46.2	46.1	48.0	47.8	44.5
900 (15)	47.8	47.4	49.4	49.0	45.9
1020 (17)	48.9	48.7	50.3	49.8	46.9
1080 (18)	49.2	49.0	50.9	50.0	47.1
1200 (20)	50.1	50.0	51.6	50.1	48.0
1260 (21)	50.6	50.1	51.9	50.4	48.2
1320 (22)	51.0	50.8	52.0	50.5	48.7
1380 (23)	51.2	51.0	52.1	50.8	48.9
1440 (24)	51.9	51.1	52.2	50.8	49.0

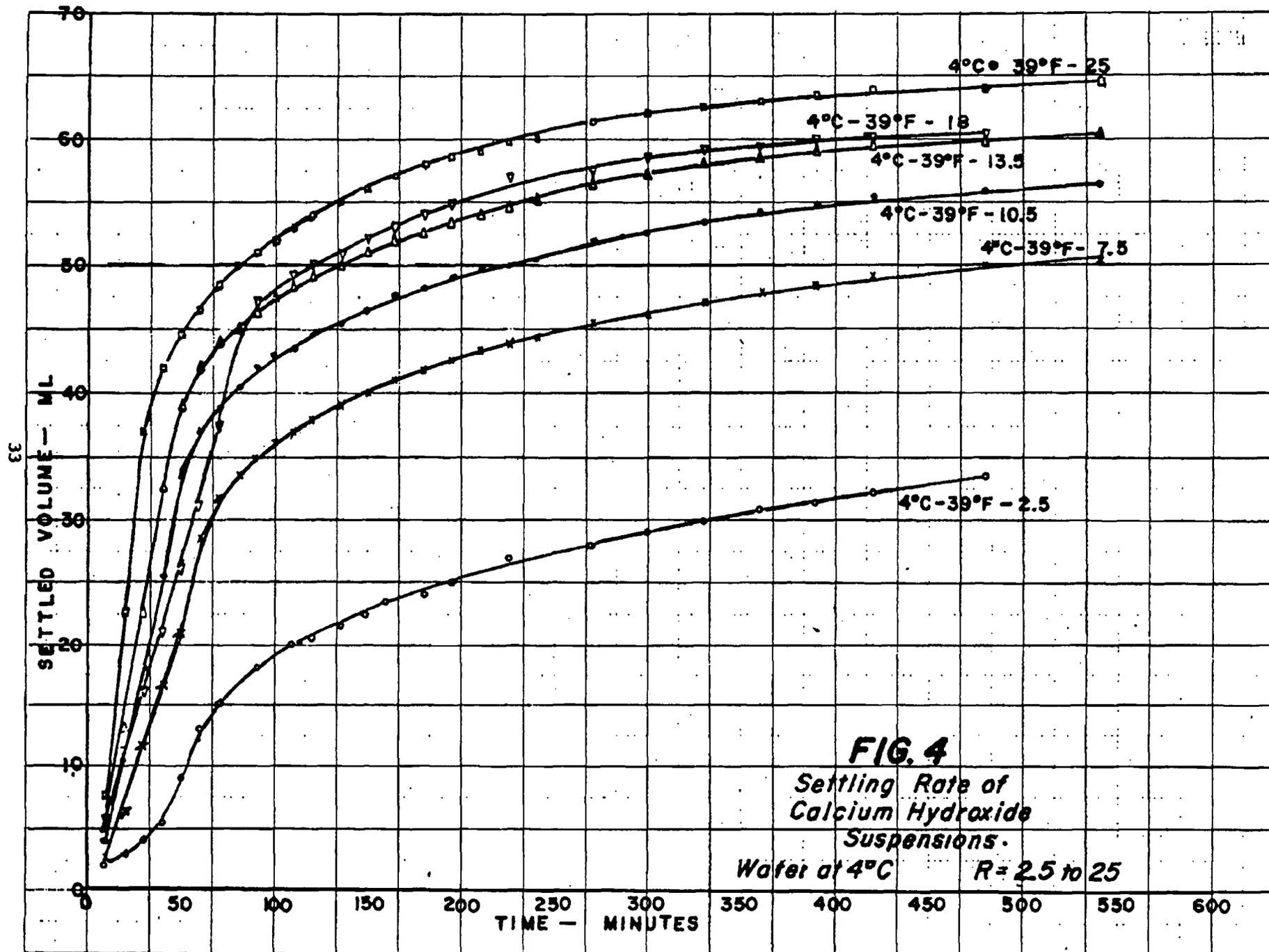


FIG. 4
 Settling Rate of
 Calcium Hydroxide
 Suspensions.
 Water at 4°C R = 2.5 to 25

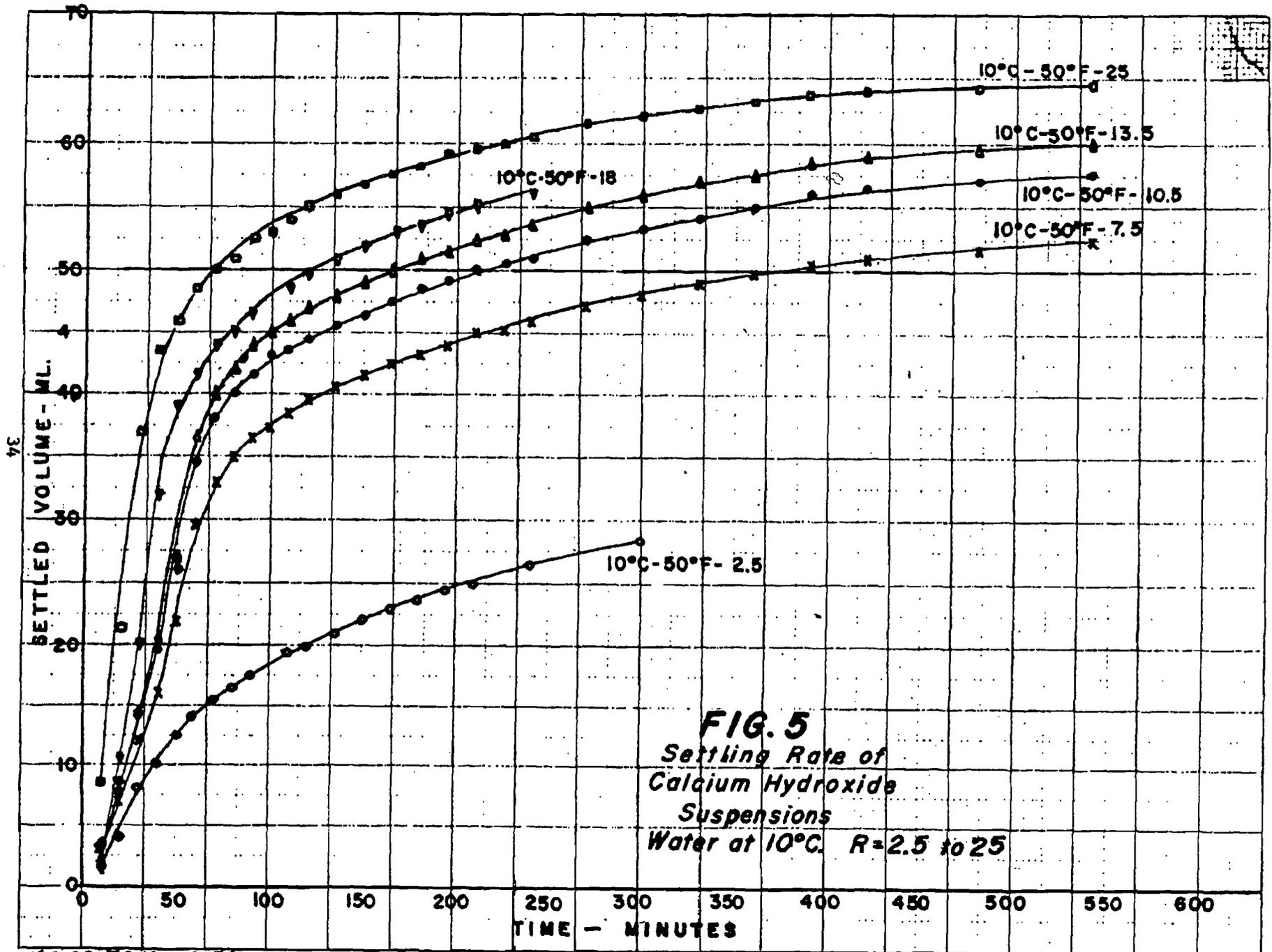


FIG. 5
*Settling Rate of
 Calcium Hydroxide
 Suspensions
 Water at 10°C. R=2.5 to 25*

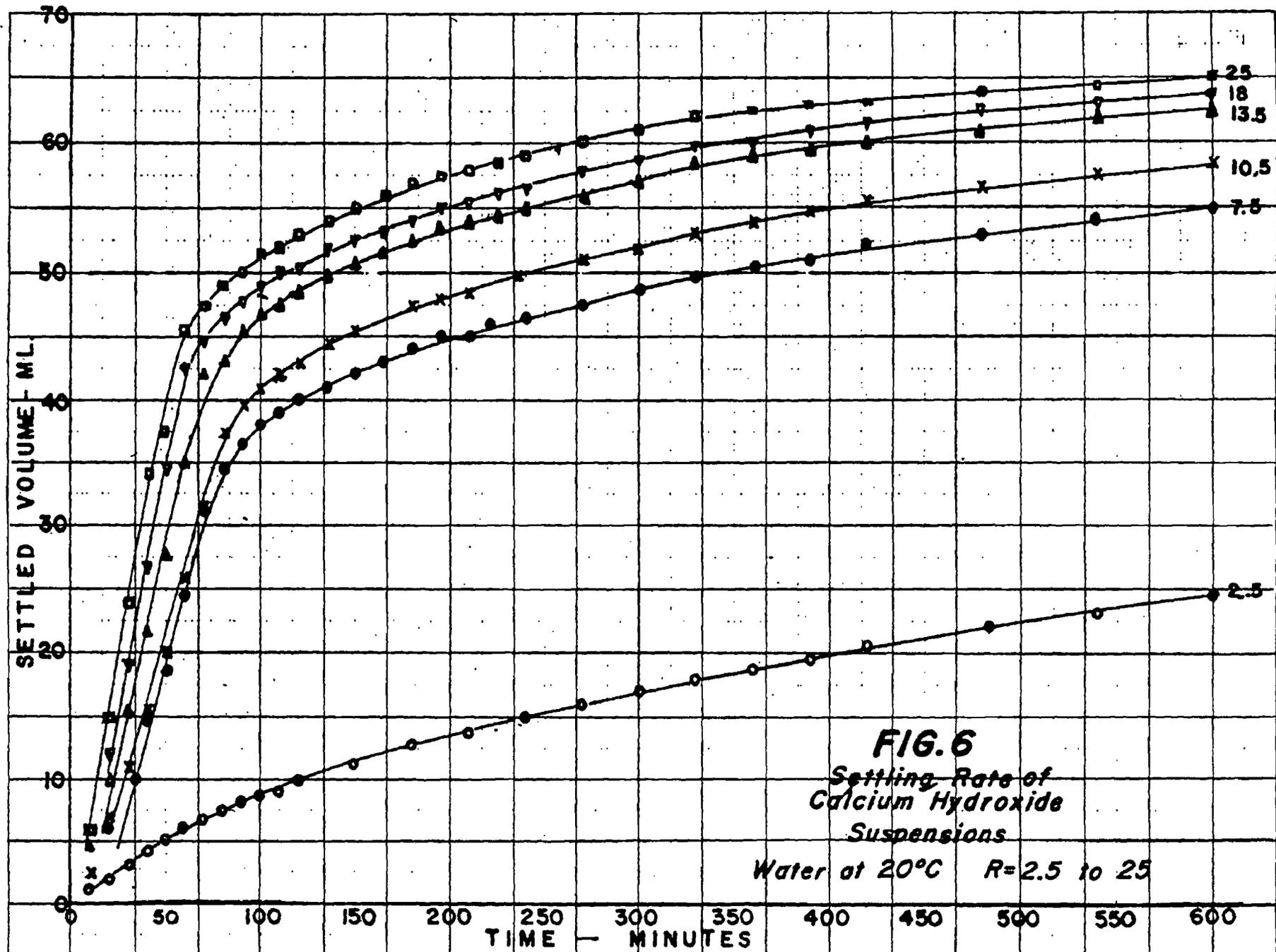
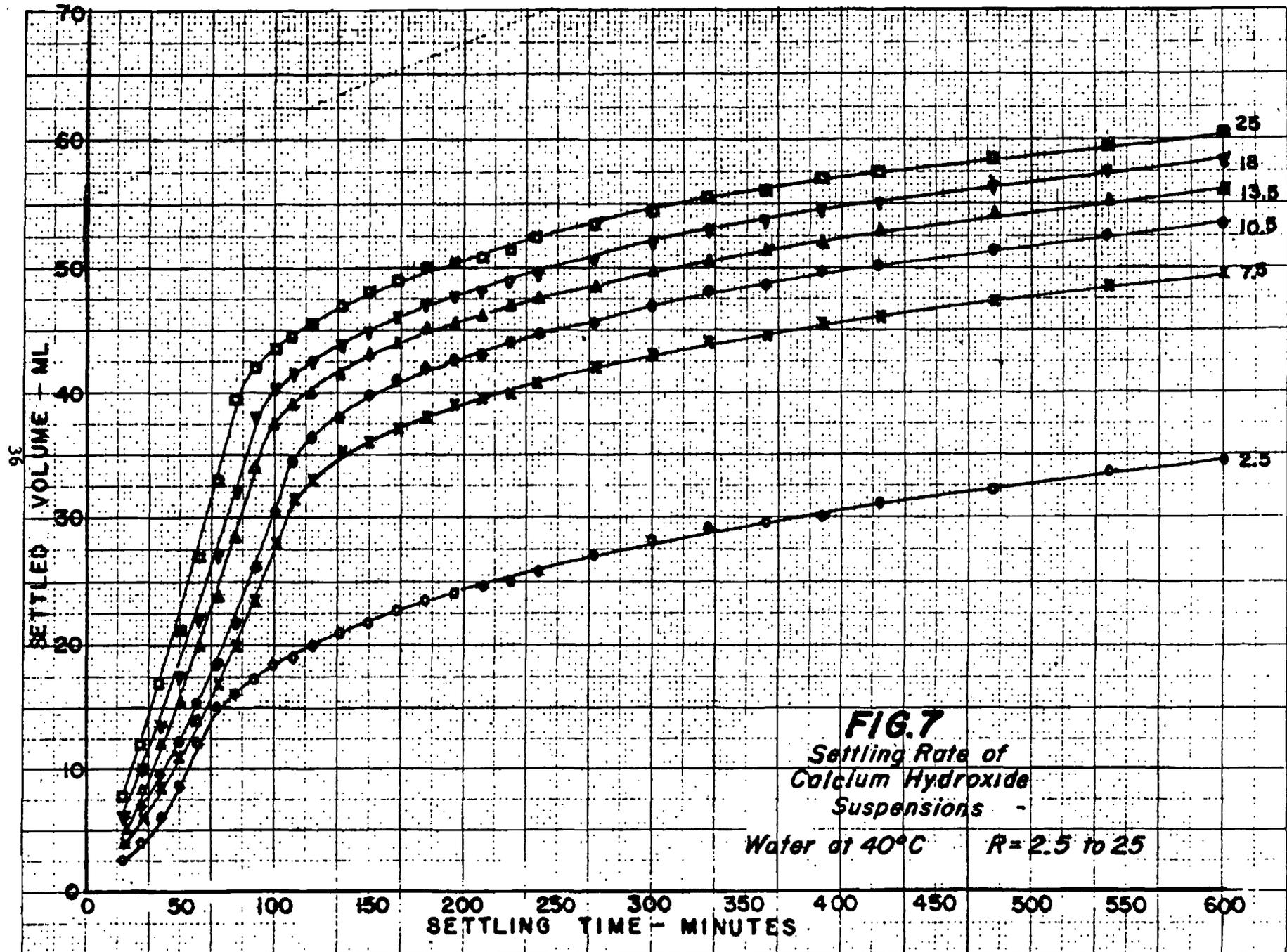


FIG. 6
*Settling Rate of
 Calcium Hydroxide
 Suspensions*

Water at 20°C R=2.5 to 25



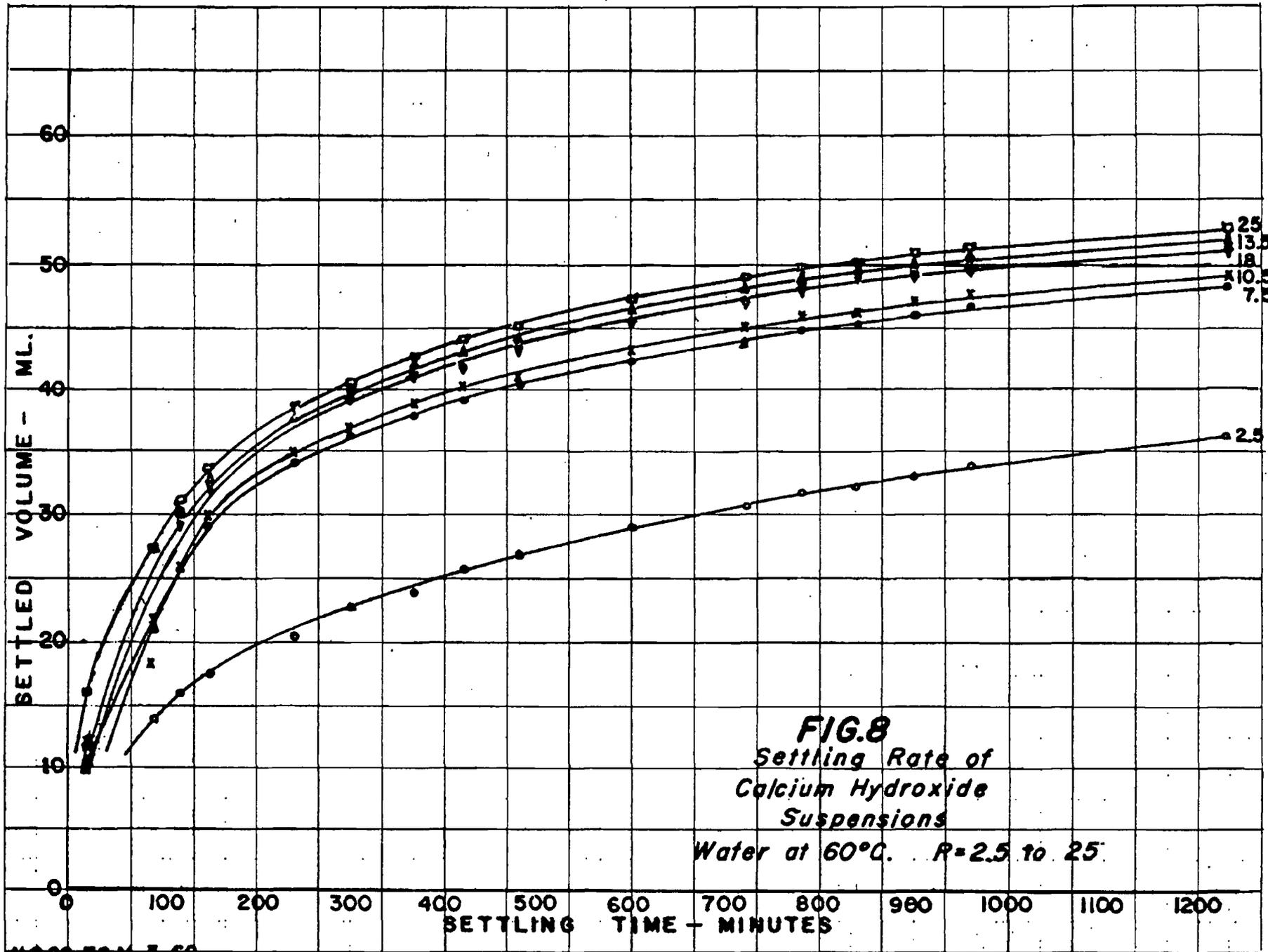


FIG. 8
Settling Rate of
Calcium Hydroxide
Suspensions
Water at 60°C. R=2.5 to 25.

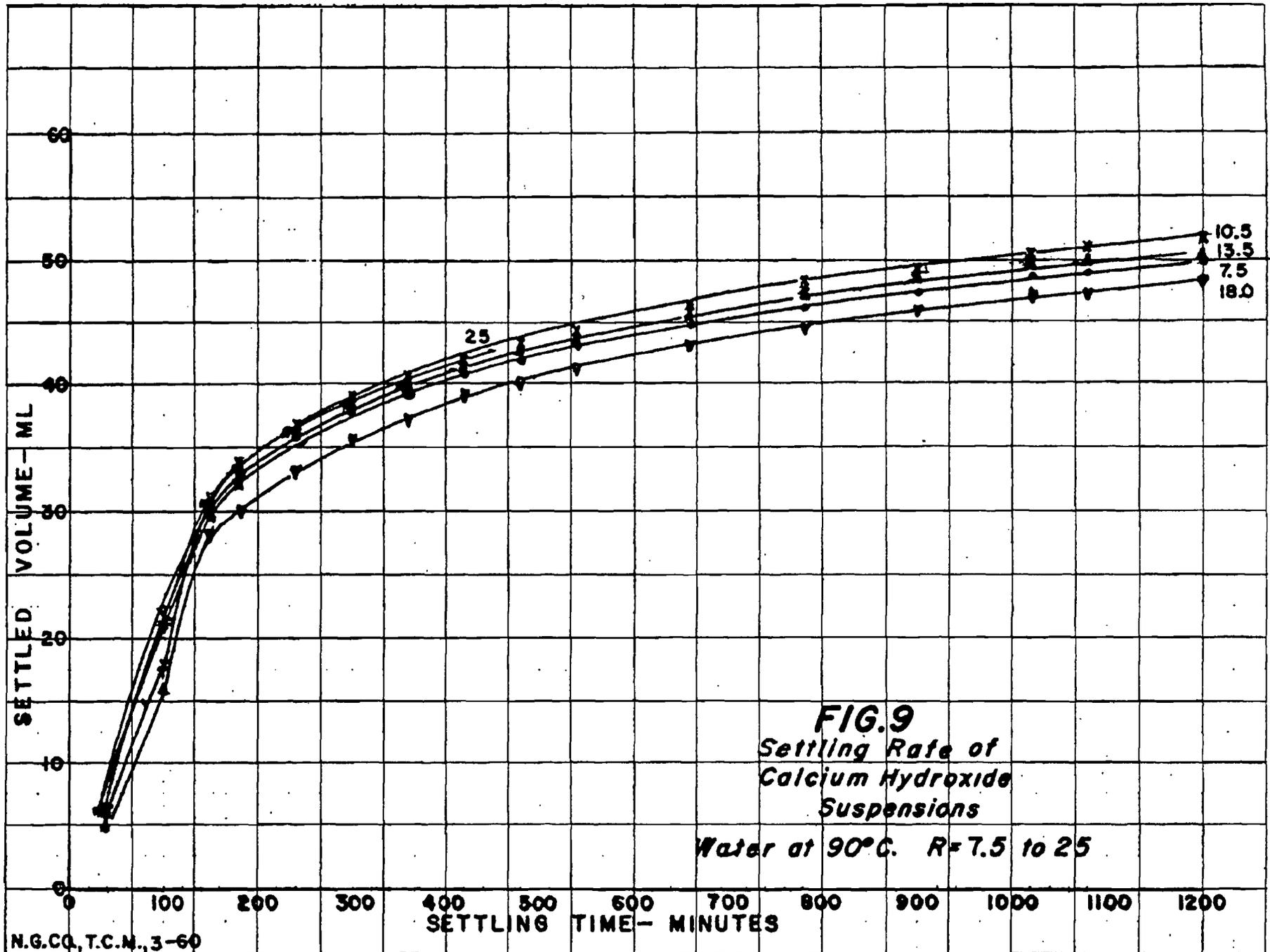


TABLE XV

SETTLING TIME OF CALCIUM HYDROXIDE

PRODUCED WITH VARIOUS RATIOS OF WATER OF DIFFERENT TEMPERATURE

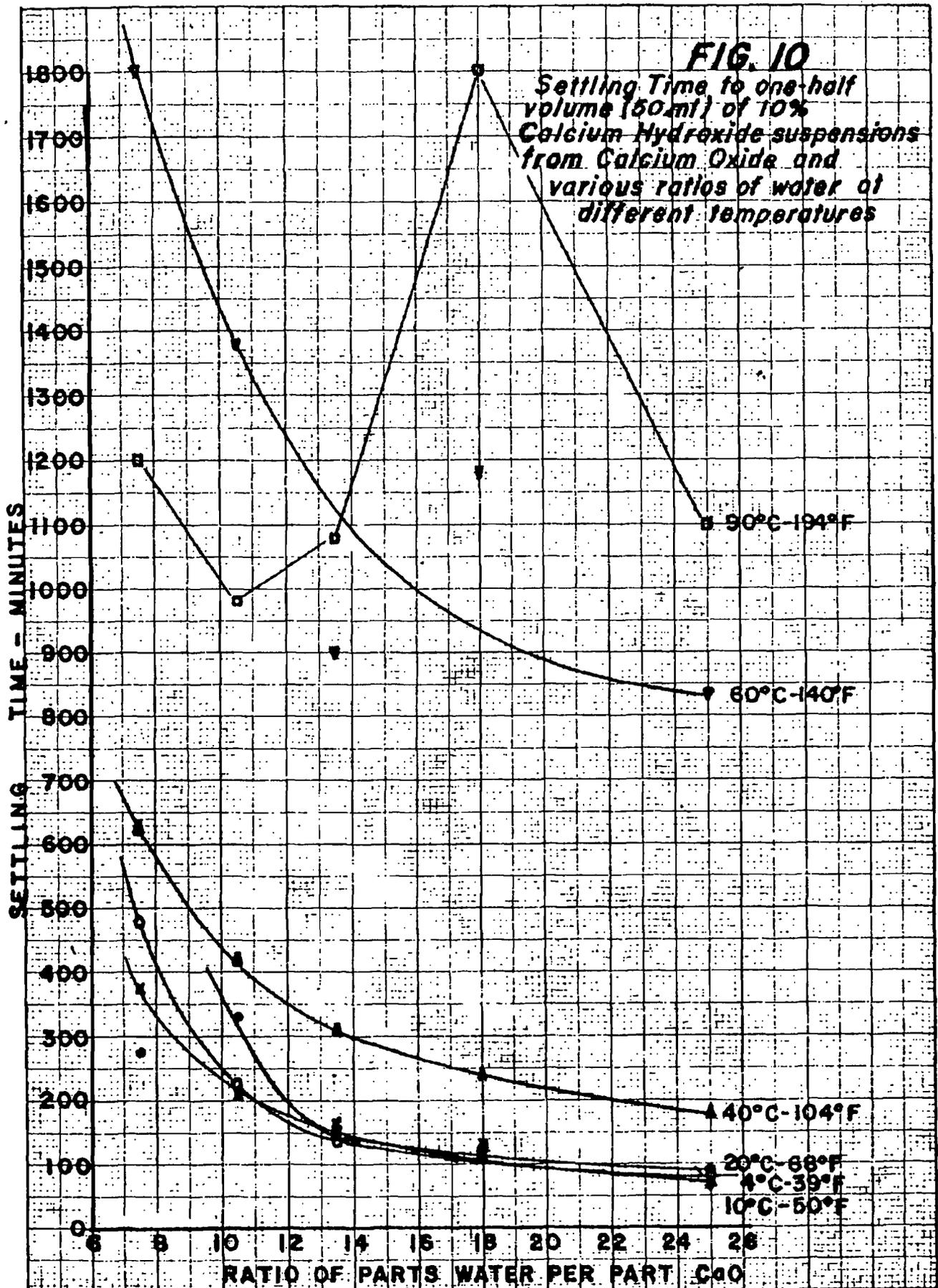
Temp. °C	4	10	20	40	60	90
°F	39	50	68	104	140	194
R(H ₂ O/CaO)	—	—	—	—	—	—
2.5						
7.5	480	375	275	630	1800	1200
10.5	225	210	330	420	1380	980
13.5	135	165	140	310	900	1080
18.0	120	126	110	240	1180	1800
25.0	80	70	90	180	835	1100

TABLE XVI

VOLUME OCCUPIED BY CALCIUM HYDROXIDE

AFTER SETTLING 10% SUSPENSION FOR 24 HOURS

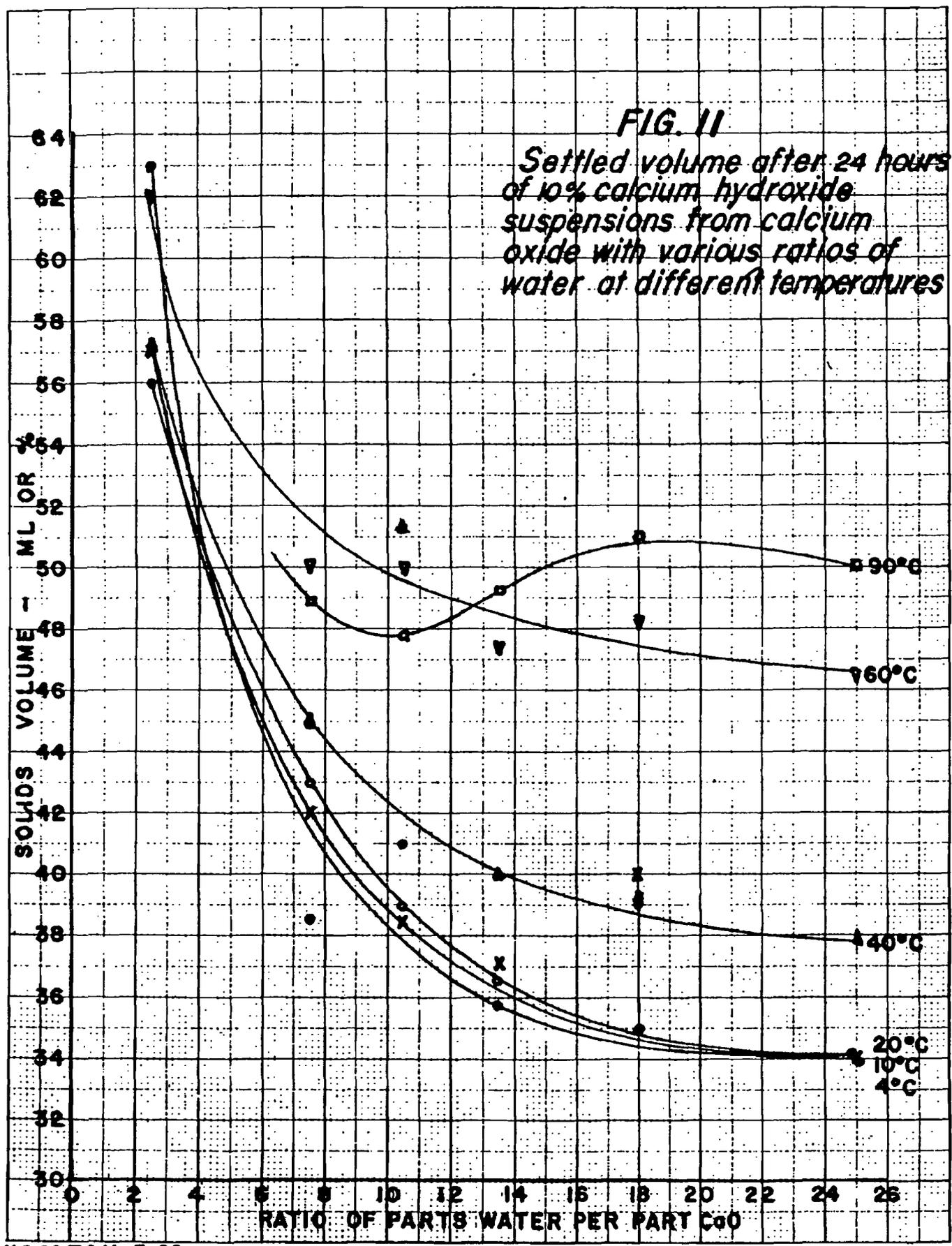
Temp. °C	4	10	20	40	60	90
°F	39	50	68	104	140	194
R(H ₂ O/CaO)	—	—	—	—	—	—
2.5	56	57	63	57	62	--
4.5	--	--	--	--	--	--
7.5	43	42	38.5	45	50.8	48.9
10.5	39	38.5	41	51.25	50	47.8
13.5	36.6	37	35.75	40	47.5	49.2
18.0	39	40	35	39	48.3	51
25.0	34	34	34	37.5	46.5	50



NG.CO.T.C.M. 3-60

FIG. 11

*Settled volume after 24 hours
of 10% calcium hydroxide
suspensions from calcium
oxide with various ratios of
water at different temperatures*



None of the calcium hydroxides prepared with a ratio of 2.5 pounds water per pound calcium oxide settled to one-half volume even after one week (10,000 minutes). The settling time values for suspensions prepared with water between 4°C and 60°C fall between those values shown for 4°C and 60°C and are of the same increasing values with decrease in R.

The settling times for suspensions prepared with water at 90°C (194°F) are more constant for all values R than any of the suspensions prepared with water at lower temperatures. Some irregularity exists with changes in R, but this difference has not been fully explained. A decrease in settling time with an increase in the value of R does not occur at this temperature. The slaking temperatures for all values of R at this temperature theoretically exceeds 212°F (Table IV) and actually evaporated some of the slaking water during the reaction. This boiling temperature undoubtedly produced crystal growth of calcium hydroxide to increase both the settling time and the viscosity.

These data indicate that the settling time of calcium hydroxide can be controlled by choosing a combination of initial water temperature between 4°C and a temperature producing a final temperature less than 212°F, and ratio of water to calcium oxide to give the desired characteristic.

C Specific Surface

The time required to adjust the suspensions to the required 100 gpl calcium hydroxide and to determine the settling time was enormous, and would be unjustified as a control test in an industrial plant requiring several periodic checks per day. A shorter and more convenient method of testing involves the determination of specific surface. The specific surface of each sample is tabulated in Table XVII and shown graphically in Figure 12. The specific surface values range from a low of 15,314 cm²/g produced with hydrating water at 4°C at R = 25 to a high of 58,300 cm²/g produced with water at 90°C at R = 2.5. These specific surface values represent a mean particle diameter range from 1.74 microns (u) to 0.46 u respectively. The calculated mean particle diameters for the calcium hydroxide produced in all samples are shown in Table XVIII.

TABLE XVII

SPECIFIC SURFACE OF CALCIUM HYDROXIDE

PRODUCED WITH VARIOUS RATIOS OF WATER OF DIFFERENT TEMPERATURES

Temp. °C	4	10	20	40	60	90
°F	39	50	68	104	140	194
<u>R(H₂O/CaO)</u>	—	—	—	—	—	—
2.5	50,736	54,293	52,790	56,606	57,355	58,300
4.5	--	--	48,307	--	52,260	55,255
7.5	35,246	34,534	--	47,035	49,183	53,070
10.5	29,133	29,840	--	45,203	48,920	51,126
13.5	23,166	24,419	36,520	41,080	45,967	52,658
18.0	17,833	18,968	31,556	37,620	48,307	53,925
25.0	15,314	18,597	29,405	40,910	48,244	53,295

TABLE XVIII

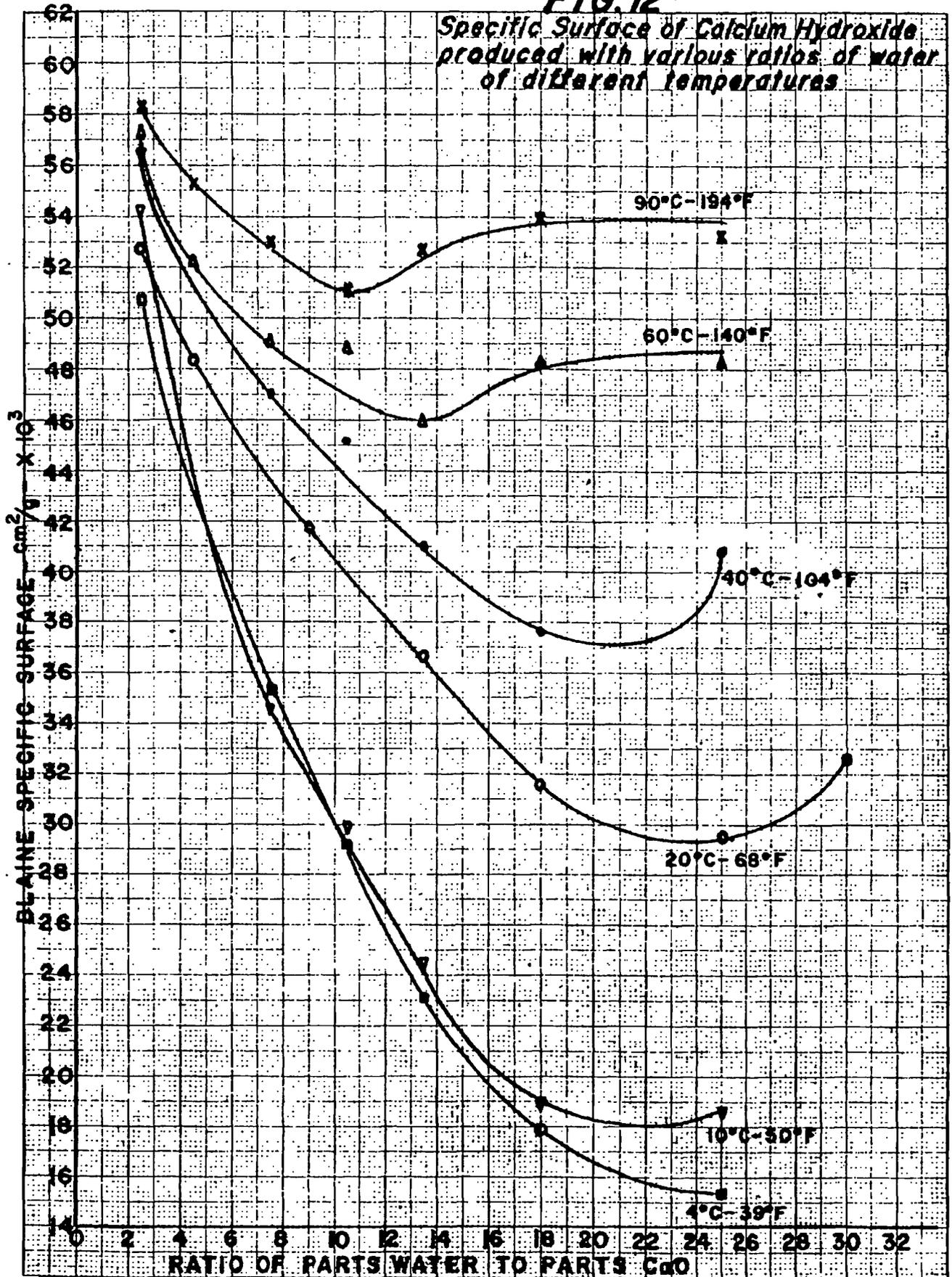
CALCULATED PARTICLE DIAMETER (MICRONS) OF CALCIUM HYDROXIDE

PRODUCED WITH VARIOUS RATIOS OF WATER OF DIFFERENT TEMPERATURES

Temp. °C	4	10	20	40	60	90
°F	39	50	68	104	140	194
<u>R(H₂O/CaO)</u>	—	—	—	—	—	—
2.5	0.53	0.49	0.50	0.47	0.46	0.46
4.5	--	--	0.55	--	0.51	0.48
7.5	0.76	0.77	--	0.57	0.54	0.50
10.5	0.91	0.89	--	0.59	0.54	0.52
13.5	1.15	1.09	0.73	0.65	0.58	0.51
18.0	1.49	1.40	0.84	0.71	0.55	0.49
25.0	1.74	1.43	0.90	0.65	0.55	0.50

FIG. 12

Specific Surface of Calcium Hydroxide produced with various ratios of water of different temperatures



An initial water temperature of 4°C (39°F) and a change in R from 2.5 to 25 pounds water to pounds calcium oxide produces calcium hydroxide with specific surfaces from 50,736 cm²/g to 15,314 cm²/g with corresponding mean particle diameters from 0.53 to 1.74 u. Settling times represented by particles of this size, according to Table IV, range from 480 minutes to 80 minutes respectively. A constant water temperature of 10°C (50°F) and R from 2.5 to 25 likewise produces calcium hydroxide of decreasing specific surfaces from 54,293 cm²/g to 18,597 cm²/g with corresponding mean particle diameter from 0.49 u to 1.43 u with increase in R. Particles of this range have settling times from 375 minutes to 70 minutes respectively. Water temperature of 20°C (68°F) follows a similar pattern with the usual change in R, but the change of a much smaller magnitude than either 4°C or 10°C.

The range of the calcium hydroxide at a water temperature of 20°C is from 52,790 cm²/g to 32,610 cm²/g specific surface with corresponding mean particle diameters of 0.50 u to 0.90 u, indicating that the higher temperature slaking water gives changes of less magnitude than at the two previous temperatures. Settling times of these samples more or less correlate this data by showing less variation of settling values from 235 minutes to 90 minutes. Water temperatures of 40°C (104°F) and 60°C (140°F) both show less mean particle size variation than the previous temperatures. At 40°C the change will be seen to be from 56,606 cm²/g to 40,910 cm²/g specific surface corresponding to mean particle diameters of 0.47 u to 0.65 u, while at 60°C the variation is from 57,355 cm²/g to 48,244 cm²/g specific surface with mean particle diameters of 0.46 u to 0.55 u. This narrow range of mean particle diameters would be expected to show longer settling time than previous series for all values of R.

Slaking water at 90°C (194°F) produces from 58,300 cm²/g to 53,295 cm²/g specific surfaces for all values of R with a mean particle diameter range of only 0.46 u to 0.50 u. Very long settling times would be expected from these suspensions. Table XIV and Figure 9 show active settling times from 980 minutes to 1200 minutes.

The specific surface decreases (mean particle diameter increases) for all initial water temperatures to 60°C as the ratio (R) of water increases from 2.5 to 25. Also, the specific surface increases (mean particle diameter decreases) for each value of R as the initial water temperature increases.

The highest specific surface calcium hydroxides were obtained from those tests producing final temperatures of or greater than 212°F. These temperatures were obtained with R at 2.5 for all initial slaking water temperatures investigated and for an initial slaking water temperature of 90°C at all values of R. The development of specific surface of a calcium hydroxide is therefore a function of the final slaking temperature. Final slaking temperatures less than 100°C (212°F) develop the specific surface of calcium hydroxide in proportion to the final temperature, which is another way of defining the ratio; R, of water. Higher ratios of water resulting in lower final temperatures produce the lower specific surfaces, and low ratios of water resulting in higher final temperatures produce higher specific surfaces. Investigating this condition further, the amount of water required for several ratios was heated to the calculated initial temperature (T₁) to result in a final temperature (T₂) approaching 100°C or 212°F (Table V), and used for slaking tests. The tabulation of data for the tests and the results of final temperature of the suspension and specific surface of the calcium hydroxide are shown in Table XIX.

TABLE XIX

Results from Volume and Temperature of H₂O (T₁) to Produce a Final Temperature (T₂) of approximately 212°F

R	Temperature °F		Specific Surface cm ² /g
	T ₁	T ₂	
2.5	57.2	210.9	55,100
7.5	167	211.1	52,300
13.5	190	211.6	51,600
25.0	205	212.7	53,200

The final temperature of each test approached the expected value of 212°F. The specific surface values are of the same magnitude. Therefore, these data offer further proof that to produce extremely high specific surface or small particle-diameter calcium hydroxide requires a high slaking temperature approaching 100°C (212°F). It is a matter of choice for the ratio of water to be used so long as the temperature calculated for this value of R will produce a final temperature approaching, but not exceeding, 212°F.

It is important that the calcium oxide have a high degree of activity to produce a high specific surface calcium hydroxide in a short slaking cycle. Otherwise, a low activity calcium oxide will increase radiation losses to reduce the slaking temperature below the necessary limit.

Very low values of R will produce high specific surface calcium hydroxide. However, at these concentrations, especially above an initial starting temperature 50°F (10°C) the final slaking temperature (T_2) will theoretically be above 212°F resulting in the evaporation of a large proportion of the water. Also, values of R at temperatures approaching 90°C (194°F) produce high specific surface calcium hydroxide. Final temperatures of these combinations will be theoretically above 212°F, so that a large amount of the slaking water will be evaporated.

Aqueous suspensions of calcium hydroxide exposed to heated bodies above 214°F have been shown to produce hexagonal crystals of fairly large size (Wire and Wire Products, October 1955). The specific surface of these suspensions increases as the crystallization increases because of the colloidal characteristics of aqueous suspensions of crystalline calcium hydroxide.

It has also been found optically that calcium hydroxide produced by the slaking of calcium oxide in water at values of R and T_1 to result in a final slaking temperature T_2 of 212°F or calculated theoretically to exceed 212°F also produces crystalline calcium hydroxide. The specific surface, settling time and viscosity of these suspensions are greatly increased because of this crystallization.

Suspensions produced at all values of R with T_1 at 194°F (90°C) contained large amounts of crystalline calcium hydroxide which account in part to the very high specific surfaces. Crystallization also increases the settling time as shown in Table XIV.

The initial slaking temperature (T_1) should be chosen to assure a final slaking temperature (T_2) of 212°F or less to prevent or reduce to a minimum the opportunity for crystal growth.

D VISCOSITY

The viscosity was determined on calcium hydroxide suspensions slaked with several ratios of water and temperatures then cooled to 70°F. Two of the suspensions were prepared at R of 7.5 and T_1 of 4°C (39°F) and 60°C (140°F). One suspension was prepared at R of 2.5 and T_1 of 14°C but was too viscous for a test. Three suspensions were prepared at R of 7.5, 13.5 and 25 and T_1 of 75°C (166.8°F), 88°C (190°F) and 96°C (205°F) respectively calculated to produce final temperatures (T_2) of 212°F. The values for T_2 and the viscosities, with the exception of the one prepared at R of 2.5, are shown in Table XX.

TABLE XX

Slaking Temperature and Viscosity (Centipoises) of Calcium
Hydroxide Suspensions

Sample	R	°C Temperatures		Viscosity
		T ₁	T ₂	
1	7.5	4	33.8	38
2	7.5	60	88.3	163
3	2.5	14	99.4	--- *
4	7.5	75	99.5	241
5	13.5	88	99.8	28
6	25.0	96	100.4	10

* Suspensions prepared at this value of R are highly viscous and a viscosity test is meaningless.

The viscosity increased with an increase in temperature for a constant water ratio. When the water ratio was increased and the initial temperature of the water increased to produce a final temperature approaching 212°F the viscosity decreased at a very rapid rate.

The theoretical concentration of a suspension at R of 7.5 is approximately 162 gpl. The concentration at R of 13.5 and 25.0 are 91.4 gpl and 49.7 gpl respectively. The concentration at R of 2.5 is theoretically 456 gpl. Therefore it would be expected to find very low viscosities of suspension prepared with R of 13 and 25 as shown in samples 5 and 6. Samples 5 and 6 were allowed to settle and the calculated amount of supernatant water decanted to give a concentration equivalent to R of 7.5. Sample 3 required diluting with water to reduce the concentration from 456 to 162 gpl. The viscosities of these corrected suspensions are shown in Table XXI.

TABLE XXI

Viscosity (Centipoises) of Calcium Hydroxide Suspensions
at approximately 177 gpl

Sample	R of Original Suspension	Viscosity of Suspension corrected to 162 gpl
3	2.5	131
4	7.5	241
5	13.5	360
6	25.0	291

The amount of water employed for slaking and its initial temperature has a decided effect on the viscosity of a calcium hydroxide during the slaking of calcium oxide. A ratio of water of 7.5 at a temperature of 75°C (167°F) produces a suspension of higher viscosity than a suspension prepared with a ratio of 13.5 even though the same final slaking temperature is reached. However, when both suspensions are made to the same concentration, the one prepared with the greater ratio of water has the higher viscosity. A suspension of calcium hydroxide prepared at a ratio of 25 and an initial temperature of 96°C does not produce the same viscosity when corrected to 162 gpl.

The viscosity of the calcium hydroxide suspensions at a concentration of 100 gpl were determined. It was anticipated the values would be relatively low at this low concentration, but it was thought that values for any differences, however slight, may help to explain some of the differences in the settling rates. The values for most of the samples produced are shown in Table XXII.

TABLE XXII

Viscosity (Centipoises) of Calcium Hydroxide Suspensions
at Concentration of 100 gpl (CaOH)₂

R	°C °F	Initial Water Temperature					
		4 39	10 50	20 68	40 104	60 140	90 194
2.5	--	--	--	72	42	63	--
7.5	35	27	21	25	32	28	
10.5	28	24	24	22	32	27	
13.5	--	23	22	20	29	26	
18.0	--	--	21	19	33	--	
25.0	--	--	20	19	--	--	

The viscosities of suspensions of this low concentration will be very low. The viscosities are higher at the lowest water ratio of 2.5. These samples are undoubtedly influenced by the presence of crystalline calcium hydroxide produced at this low water ratio. The viscosity decreases with an increase in the water ratio between 39°F and 104°F. The viscosity appears constant at ratios from 7.5 to 18 for initial water temperatures of 60°C (140°F) and 90°C (194°F).

The higher viscosities of suspensions prepared with water ratios of 2.5 indicate a change in physical properties which will decrease the settling time. Therefore, the settling time is not dependent upon mean particle diameter (or specific surface) of the suspended calcium hydroxide alone.

VII CONCLUSIONS

This preliminary study of the reaction between calcium oxide and water reveals the complexity of the reaction in producing results regarding settling time, specific surface and viscosity of calcium hydroxide suspension prepared with an excess of water.

Advantage can be taken of the thermodynamics of the reaction by altering the ratio and temperature of water per pound of calcium oxide to produce calcium hydroxide varying in particle diameter from fairly large to extremely small as determined by the Blaine air permeability method. Low ratios of water produce higher reaction temperatures and calcium hydroxide of high specific surfaces. Specific surfaces vary less with changes in water temperatures at low water ratios. Specific surfaces also vary less with water at high temperatures for all ratios. The specific surface of the calcium hydroxides vary over a very wide range at ratios of 7.5 to 25 and at temperatures from 4°C (39°F) to approximately 60°C (140°F).

Settling times of calcium hydroxide suspensions corrected to 100 gpl do not correlate changes in ratios and temperature of water as well as specific surface measurements. This may be caused by the influence of the viscosity of a suspension on the settling rate of the particles of calcium hydroxide. A considerable change in viscosity was found which has not been fully explained.

This study, although presenting encouraging data on specific surface control, indicates the need for more information on the factors influencing the difference in the rate of settling and a more thorough knowledge of particle size distribution with changes in the process.

Data on the control of specific surface or mean particle diameter by either a change in the ratio of water to calcium hydroxide or a change in the temperature of water at any given ratio of water to calcium hydroxide is presented which, to our knowledge, has not been previously available to the chemical industry. A better understanding of this principle offers the industry a new method of more consistent control at higher efficiency.