

A Model for the Kinetics of the Hardening of Portland Cement

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A formula is proposed that describes the kinetics of the hardening process of a portland cement as a function of the C_3S content and C_3A content. The formula is the mathematical expression of a simple cement model which consists only of two hardening components and satisfies several logical conditions. The properties of the model and derivation of the formula are presented. The values calculated by the new formula are compared to experimental values of compressive, tensile, and flexural strengths published earlier, and it is concluded that the equation is applicable for the kinetics of the hardening of a large group of air-entrained and non-air-entrained portland cements with reasonable accuracy. It is also found that the specific rate of strength development can be considered as a linear function, and the specific deceleration of the strength development as a quadratic function of the C_3A content of the cement.

THE technical literature contains several proposals for the relationship between the composition of portland cement and its strength and hardening, respectively. Gonnerman was probably the first who attempted to express the strength of a portland cement mortar as a function of the four main clinker minerals for various age groups. He used a linear relationship (1). Among the other proposals (2, 3, 4) perhaps the following empirical formula is the most popular:

$$s = c_1 \log t + c_2 \quad (1)$$

where

t = age of specimen;

s = strength of specimen at a given age; and

c_1 and c_2 = factors independent of the age but dependent on the type of cement, curing, testing conditions, etc.

Values calculated by Eq. 1 can be represented by a straight line in an s vs $\log t$ semilogarithmic system (5, 6, 7). This formula is the mathematical expression of the assumption that the rate of hardening is inversely proportional to the age of the specimen; that is, the product of the age and the rate of hardening at that age is assumed to be the c_1 constant. A weakness of this proposal is that it postulates an indefinite increase in strength with the increase in age which is obviously incorrect. The other proposals are not satisfactory either for one reason or another. It may also be mentioned that an excellent study was published recently on the kinetics of the hydration of calcium silicates (8), and another on the kinetics of the hydration of portland cement (9). However, neither of these discusses the strength development.

In this paper a formula is proposed that describes the kinetics of the hardening process of a portland cement as a function of the C_3S content and C_3A content. This formula is the mathematical expression of a cement model. It will be shown that the strengths

provided by an appropriate form of this cement model at various ages are close to the strengths of a given portland cement. The properties of the model are as follows:

1. It consists only of two hardening components; the first component is the C_3S , and the second is a mixture of the other cement ingredients.
2. These two components hydrate simultaneously with differing rate but without any interaction, except that the C_3A , which is a part of the second component, may affect the rate of hardening of the C_3S . Since, however, the C_3S does not affect the strength resulting directly from the C_3A in the model, the strengths of the C_3S and the second component can be superimposed.
3. The s_0 final strength of C_3S , resulting theoretically from an infinitely long curing, is the same as the final strength of the second component.
4. The decelerations of the hardening of both the C_3S and the second component at a given age are proportional to the $(s_0 - s)$ remaining strength development at that time, but the two proportionality factors are different.
5. The proportionality factors may be functions of the C_3A content.

Thus, this model, in accordance with the technical meaning of the term "model" (10), resembles a portland cement in several but not in all respects; for instance, the composition of the model is simpler. More specifically, Condition 1 is a simplification which, however, implies the empirical observation of several investigators that there is a correlation between the strength of portland cement and its C_3S content (1, 11). Condition 2 assumes that the fractional rate of hydration of the components, with the exception of C_3S , of a given cement is the same. This is again a simplification that contradicts the observation (9). It can be regarded as a modification of the hypothesis developed (and rejected) by Copeland and Bragg that the fractional rate of hydration of all components of a given cement is the same. As far as Condition 3 is concerned, experimental data by Bogue and Lerch show that the final strengths of C_3S and C_2S are practically the same (12). Condition 4 is a working hypothesis. The gradual reduction of the rate and deceleration of the hardening can be visualized as the effect of the hydrated cement that hinders the further hardening in the specimen. Finally, in accordance with experimental data (13, 14, 15, 16), Condition 5 expresses the fact that the C_3A has a more pronounced role in the hardening of portland cement than its direct contribution to the strength which would follow solely from the hardening of C_3A .

It appears feasible to construct an electrical or mechanical model that complies with the foregoing five conditions. Such a model could then be used as an analog computer for the computation of the hardening process of a portland cement.

It is not claimed that the paper contributes to the scientific side of the hydration of portland cement. Nevertheless, it appears to have certain merits. First, it deals with strength which is one of the most important technical properties; second, the applied method is a novel one which might have further useful application in the future; and third, the proposed model represents a solution which appears superior in several respects to the comparable solutions available in the technical literature.

THE NEW FORMULA AND ITS DERIVATION

The general form of the proposed formula can be obtained from the fourth condition above. The mathematical expression of this condition applied, say, to the C_3S is the following differential equation:

$$-\frac{d^2s_1}{dt^2} = a_1^2 (s_0 - s_1) \quad (2)$$

where

- t = age of specimen at testing;
- s_1 = strength of C_3S in the cement paste at a given t age;
- s_0 = strength of C_3S after infinitely long curing;
- a_1 = parameter which is independent of the strength and age but may be a function of the fineness and composition of the cement, composition of the specimen, curing and testing methods, etc. —when the age is expressed in days, the unit for the a factor is 1/day.

If the boundary conditions that $s_1 = 0$ when $t = 0$, and $s_1 = s_0$ when $t = \infty$ are applied, then the solution of Eq. 2 can be written as follows:

$$s_1 = s_0 \left(1 - e^{-a_1 t} \right) \quad (3)$$

A similar relationship can be obtained for the hardening of the second component with an a_2 parameter. Thus, it follows from the second and third conditions that the s strength of a portland cement will be expressed by the following:

$$s - s_0 \left[p \left(1 - e^{-a_1 t} \right) + (1 - p) \left(1 - e^{-a_2 t} \right) \right] \quad (4)$$

where p designates the relative amount of C_3S in the cement (percentage/100).

Three comments should be made: (a) it will be shown that the a parameters represent the specific rates of hardening for the two components of the model; (b) the form of Eq. 4 is very similar to the formula which characterizes a certain rheological model and which is frequently used for the description of basic creep of concrete (17); and (c) the hyperbolic form recommended by Goral (3) for the s vs t relationship can be obtained from Eq. 3 by expansion into a series.

EXPERIMENTAL VERIFICATION OF THE MODEL

Eq. 4 is not directly suitable for practical calculations because it contains the s_0 final strength of the portland cement which seems a function of several variables and is usually unknown. Therefore, it is expedient to transform Eq. 4 and express the $s_{rel} = S$ relative strength in a dimensionless form rather than the actual strength. If the basis of this relative strength is the 28-day strength, then

$$S = s_{rel} = 100 s/s_{28} = 100 \frac{p \left(1 - e^{-a_1 t} \right) + (1 - p) \left(1 - e^{-a_2 t} \right)}{p \left(1 - e^{-28a_1} \right) + (1 - p) \left(1 - e^{-28a_2} \right)} \quad (5)$$

$$= 100 \frac{1 - pe^{-a_1 t} - (1 - p)e^{-a_2 t}}{1 - pe^{-28a_1} - (1 - p)e^{-28a_2}} \quad (6)$$

which does not contain the value of s_0 .

One can return to actual strength values from the relative strengths with the knowledge of the strength at any age. If this strength is the 28-day strength, then Eq. 5 or 6 can be used directly; otherwise the formulas should appropriately be transformed. Such transformed formulas are applicable, at least in principle, for the estimation of the, say, 28-day strength from the strength determined at the age of 1 day or 3 days. It should be emphasized, however, that this paper investigates the kinetics of the hardening for the purpose of which relative strength values are suitable. Also, the s/s_{28} ratio is far less sensitive than the s actual strength to variations in burning and cooling conditions, as well as differences in the mineralogical composition of the raw materials used in the cement making which factors may affect the hardening process of a cement (18). Moreover, the use of relative values is not unusual in material research. For instance, the Ramberg-Osgood stress-strain diagram (18), or a study by Hansen (19) can be mentioned where the concept of a relative modulus of elasticity is utilized advantageously.

As it has been mentioned in connection with Eq. 2, the numerical values of the a parameters are influenced by numerous variables. Therefore, only the results of such tests should be used for the experimental verification of Eq. 6 where the compound composition of the portland cement is the sole variable; that is, where the fineness, gypsum content, curing and testing methods, etc., are practically identical. Several such experiments are discussed.

Gonnerman's Experiments on Mortars

A relevant investigation on mortars of 71 different portland cements was published by Gonnerman (1) as early as 1934. The range of composition of these cements was purposely expanded beyond that of normal portland cements but all the cements had an identical SO_3 content of 1.8 percent, by weight, and fineness of approximately $1,580 \text{ cm}^2/\text{g}$ (Wagner). Based on the test results, he also presented an empirical method for the calculation of mortar strength from the compound composition of portland cement.

There are three series in Gonnerman's tests that can be used for the verification of Eq. 6. In two of them the compressive strength of the various portland cements was determined with 2-in. plastic mortar cubes of 1:2.75 and 1:4.25 mixes by weight (water-cement ratios were 0.53 and 0.80 by weight, respectively). In the third series, the tensile strength of the cements was tested with 1:3 standard sand briquets. All the specimens were exposed continuously to moisture. The strength tests were performed at ages of 1, 3, 7, and 28 days, 3 months, 1 and 2 years.

An analysis of Gonnerman's test results indicated that a_1 and a_2 can be expressed as a function of the C_3A content of the portland cement. In his particular case, these a values obtained by stepwise approximation are presented below.

1. For the compressive strength of the 1:2.75 mortars:

$$a_1 = 0.0067 \text{ C}_3\text{A} + 0.10 \quad (7)$$

$$a_2 = 0.0018 \text{ C}_3\text{A} + 0.005 \quad (8)$$

where C_3A represents the percent of the potential tricalcium aluminate in the portland cement computed according to the Bogue method (21).

2. For the compressive strength of the 1:4.25 mortars:

$$a_1 = 0.005 \text{ C}_3\text{A} + 0.10 \quad (9)$$

$$a_2 = 0.001 \text{ C}_3\text{A} + 0.007 \quad (10)$$

3. For the tensile strength:

$$a_1 = 0.04 \text{ C}_3\text{A} + 0.65 \quad (11)$$

$$a_2 = 0.007 \text{ C}_3\text{A} + 0.04 \quad (12)$$

These equations show that the value of a_1 is about 7 to 10 times higher than a_2 for these mortars within the usual range of C_3A content. Accordingly, a portland cement hardens as if the C_3S develops the full value of its compressive strength by the age of about 7 days. After that any further strength increase appears to be due only to the hardening of the second component. It may also be noted that the suitable a_1 and a_2 values are much higher for the tensile strength than the corresponding values for the compressive strength. This appears to mean that the van der Waals forces which supposedly provide the main source of the tensile strength, develop their full value much more quickly in the cement paste than do the chemical bonds. If this is actually true, it would be interesting to speculate why it is so.

The form of Eqs. 7 through 12, however, is much more important than the numerical values of the coefficients because the latter are valid, strictly speaking, only for the circumstances used by Gonnerman. The form, however, reflects the effect of C_3A with respect to the kinetics of the hardening. Namely, it reveals that the specific rate of hardening is a linear function, and, consequently, the specific deceleration of hardening is a quadratic function of the C_3A content with a reasonable degree of approximation. This relation is not restricted to the C_3A . It seems also applicable to many other factors that influence the hardening of portland cement, such as the fineness of cement and the curing temperature. If a change in any of these factors increases the early strength by increasing the specific rate of hardening, then, simultaneously, the same factor increases the deceleration of the hardening to a higher degree thus the final relative strength will be less.

TABLE 1
EXPERIMENTAL AND CALCULATED RELATIVE COMPRESSIVE STRENGTHS OF 1:2.75 MORTARS^a

Cement No.	C ₃ S (%)	C ₃ A (%)	Relative Compressive Strength (%)												
			1 Day		3 Day		7 Day		28 Day	3 Months		1 Year		2 Year	
			Exp	Cal	Exp	Cal	Exp	Cal		Cal	Exp	Cal	Exp	Cal	Exp
1	43	18	16.7	13.3	43.9	33.6	63.4	58.8	100	120.2	122.7	114.2	125.1	121.7	125.1
1 Dupl	45	20	13.2	14.1	46.4	35.2	68.7	60.6	100	115.3	119.6	109.2	121.2	111.2	121.2
2B	47	16	11.5	13.3	34.3	33.9	56.0	59.5	100	108.5	122.9	125.4	126.1	115.2	126.1
2B Dupl	42	15	11.1	12.5	33.2	32.2	55.8	57.3	100	135.9	126.4	124.5	130.6	127.0	130.6
3B	43	11	10.3	11.6	28.2	30.3	45.0	55.2	100	144.1	131.9	155.0	140.4	150.2	140.4
3B Dupl	43	11	11.2	11.6	29.2	30.3	46.5	55.2	100	141.1	131.9	154.4	140.4	149.6	140.4
4	43	7	10.5	10.7	27.1	28.3	46.4	53.1	100	136.0	137.0	145.5	155.0	151.0	155.1
5B	39	2	9.4	9.3	27.2	25.4	38.2	49.4	100	168.4	142.5	194.3	193.1	208.0	198.1
5B Dupl	51	2	12.5	9.9	37.8	26.9	57.6	51.9	100	148.0	130.4	171.8	164.9	182.3	168.3
6	41	0	8.5	9.1	28.7	24.9	43.0	49.1	100	194.0	135.0	214.9	195.8	233.0	213.1
7	42	0	7.3	9.1	28.6	25.0	44.4	49.2	100	174.1	134.0	203.5	192.8	215.0	209.5
8 ^b	27	15	8.2	10.3	27.4	26.9	41.8	49.9	100	148.4	136.8	152.0	142.6	157.9	146.6
8 Dupl	42	15	9.5	12.4	30.1	31.9	54.9	56.9	100	134.1	127.0	112.2	131.3	143.6	131.3
9 ^b	53	7	10.3	11.4	30.6	30.3	48.5	56.1	100	135.1	128.3	141.1	141.9	138.1	142.0
10 ^b	56	3	9.5	10.4	34.2	28.1	51.6	53.6	100	147.4	127.0	148.2	151.9	153.0	153.4
11	51	0	9.2	9.4	37.3	25.7	57.8	50.4	100	137.2	126.6	148.5	169.6	152.4	181.8
12	41	12	10.8	11.6	29.1	30.2	48.4	55.0	100	128.2	131.9	135.3	139.4	131.3	139.4
13	38	7	6.8	10.2	22.3	27.2	44.0	51.4	100	147.1	141.9	165.0	162.4	173.0	162.6
14	37	7	8.6	10.1	28.9	27.0	51.9	51.0	100	130.1	143.0	152.2	164.0	159.5	164.2
15	48	4	6.5	10.3	27.3	27.7	47.8	52.7	100	122.9	134.0	149.0	161.2	150.0	162.1
16	42	9	12.1	11.0	31.2	29.1	50.7	53.8	100	128.3	135.4	138.8	148.1	147.1	148.2
17	39	3	7.0	9.5	29.6	25.8	51.3	49.9	100	154.7	143.4	179.0	185.9	184.2	188.4
18	43	5	9.2	10.2	31.3	27.3	49.6	52.0	100	139.4	138.7	160.4	164.8	167.3	165.4
19	44	0	6.3	9.2	27.9	25.2	46.7	49.5	100	161.9	132.2	195.0	187.0	210.8	202.6
20	42	12	7.0	11.7	25.9	30.5	48.8	55.4	100	124.7	131.2	124.2	138.5	121.0	138.5
21	40	10	7.7	11.0	30.9	29.0	54.0	56.6	100	131.7	135.7	142.6	146.8	131.9	146.8
22	41	8	7.2	10.7	27.1	28.4	49.1	52.9	100	119.4	137.6	146.8	153.4	141.3	153.4
23	38	5	7.7	9.8	25.8	26.4	47.8	50.5	100	155.3	144.1	177.5	174.2	183.0	174.8
24	41	7	8.9	10.5	30.4	27.9	45.1	52.4	100	144.1	138.9	153.2	157.9	151.2	158.0
25	44	4	7.7	10.0	28.9	27.0	47.8	51.7	100	148.4	138.0	144.7	168.6	136.0	169.6
26	42	3	7.4	9.7	26.2	26.2	43.1	50.6	100	150.5	140.0	166.0	178.8	177.4	181.1
27	41	1	6.9	9.3	28.3	25.3	47.3	49.5	100	154.8	138.3	172.1	193.4	174.0	202.6
28	44	11	11.7	11.7	31.6	30.5	52.6	55.6	100	132.1	131.1	132.1	139.5	146.0	139.5

29	40	11	7.5	11.3	25.5	29.5	47.9	54.1	100	135.0	134.2	151.5	143.4	148.0	143.4
30	39	13	7.7	11.6	28.3	30.1	53.0	54.6	100	131.8	131.9	141.8	138.4	134.3	138.4
31	49	11	13.0	12.2	33.1	31.8	53.8	57.5	100	136.0	127.5	132.5	134.8	140.4	134.9
32	36	10	9.6	10.6	26.2	27.9	42.4	52.0	100	126.2	139.2	133.3	151.4	138.1	151.4
34	41	11	9.8	11.4	26.4	29.7	44.2	54.5	100	127.4	133.4	138.5	142.4	133.9	142.4
35	41	11	10.9	11.4	30.4	29.7	44.1	54.5	100	129.0	133.4	138.0	142.4	148.2	142.4
37	16	16	8.9	8.6	19.0	23.0	34.3	44.5	100	153.9	142.5	154.9	148.5	160.0	148.5
38A ^b	61	14	11.9	14.3	40.4	36.5	67.9	63.5	100	110.2	117.4	112.4	120.5	—	120.5
39A	31	11	10.2	10.2	23.7	26.9	38.6	50.2	100	152.6	141.8	163.4	153.1	—	153.1
40 ^b	55	11	12.8	12.8	34.6	33.2	60.6	59.5	100	112.3	123.4	129.3	129.7	131.3	129.7
41	29	7	8.1	9.3	22.6	24.9	38.7	47.8	100	167.5	152.2	177.2	177.9	166.2	178.1
42	61	7	12.1	12.0	39.1	31.6	62.9	58.1	100	128.5	122.4	142.1	132.9	130.1	133.0
43	24	3	7.2	8.3	20.4	22.6	28.4	44.8	100	190.0	165.7	232.0	232.0	242.8	235.9
44	59	3	11.5	10.5	43.6	28.4	67.4	54.1	100	137.2	124.7	165.3	147.2	172.0	148.5
45	28	0	5.9	8.5	22.0	23.3	36.2	46.4	100	221.6	151.5	256.1	247.6	248.1	274.8
46	56	0	11.0	9.5	39.0	26.0	58.8	50.9	100	127.0	123.3	139.8	159.2	153.1	169.4
47	48	15	14.3	13.2	39.0	33.7	63.8	59.3	100	122.1	123.5	119.5	127.2	121.8	127.2
48	45	13	8.9	12.3	31.4	31.8	56.2	57.1	100	121.8	127.8	121.4	133.5	131.4	133.5
49	51	9	10.3	11.9	31.3	31.1	58.6	56.9	100	115.8	128.1	115.2	138.2	115.0	138.2
50 ^b	47	4	10.5	10.2	34.6	27.5	55.6	52.5	100	173.5	135.0	220.0	163.0	224.0	164.0
51	38	2	7.6	9.3	30.6	25.2	48.0	49.2	100	186.0	143.7	220.0	195.9	218.7	201.1
53 ^b	47	10	11.5	11.8	29.4	30.7	57.4	56.2	100	126.0	130.1	142.2	139.4	148.0	139.4
54	48	10	10.9	11.9	33.1	31.0	56.5	56.5	100	121.0	129.3	113.7	138.4	119.6	138.4
57	45	15	14.3	12.8	40.1	32.8	62.5	58.1	100	143.2	125.2	137.7	129.2	—	129.2
58 ^b	62	14	13.1	14.5	38.6	36.7	68.2	63.9	100	106.1	116.9	103.3	119.9	109.3	119.9
59	52	6	10.6	11.1	33.0	29.5	51.6	55.1	100	125.9	129.8	132.2	146.5	145.0	146.8
60	55	7	16.3	11.6	37.4	30.6	58.5	56.6	100	132.7	126.8	133.0	139.5	—	139.6
60A	57	6	12.4	11.4	41.2	30.3	60.2	56.3	100	135.0	125.8	137.5	140.2	—	140.4
61	56	0	10.0	9.5	37.6	26.0	58.4	50.9	100	133.0	123.3	154.8	159.2	169.1	169.4
62 ^b	74	0	11.4	9.8	48.3	26.8	74.1	52.3	100	127.0	114.4	140.0	131.4	—	136.3
100 ^b	58	17	11.3	15.0	38.0	37.6	62.0	64.4	100	95.0	116.5	86.1	118.5	—	118.5
101	56	10	13.4	12.6	34.6	32.7	61.0	59.1	100	105.4	123.7	102.1	130.9	—	130.9
102 ^b	64	17	18.1	15.7	50.0	39.2	79.8	66.6	100	105.0	113.8	95.0	115.5	—	115.5
103 ^b	66	11	12.7	13.8	39.9	35.4	69.4	62.8	100	117.9	116.8	102.0	121.2	—	121.2
104 ^b	62	20	6.7	16.5	33.6	40.6	60.0	67.6	100	103.5	112.7	88.6	113.8	—	113.8
105 ^b	60	12	8.7	13.6	31.7	34.9	49.3	61.8	100	126.0	119.5	127.2	124.0	—	124.0
106 ^b	63	17	14.3	15.6	43.7	39.0	67.5	66.2	100	101.7	114.3	—	116.0	—	116.0
108 ^b	70	5	11.8	11.7	37.2	31.2	55.0	58.0	100	122.0	117.2	—	127.9	—	128.1

^aThe Exp experimental values were obtained from Gonnerman's experiments (1); the Cal calculated values were obtained by Eq. 6 with the following factors: $\alpha_1 = 0.0067 C_3A + 0.1$ and $\alpha_2 = 0.0018 C_3A + 0.005$.

^bThese cements were double burned.

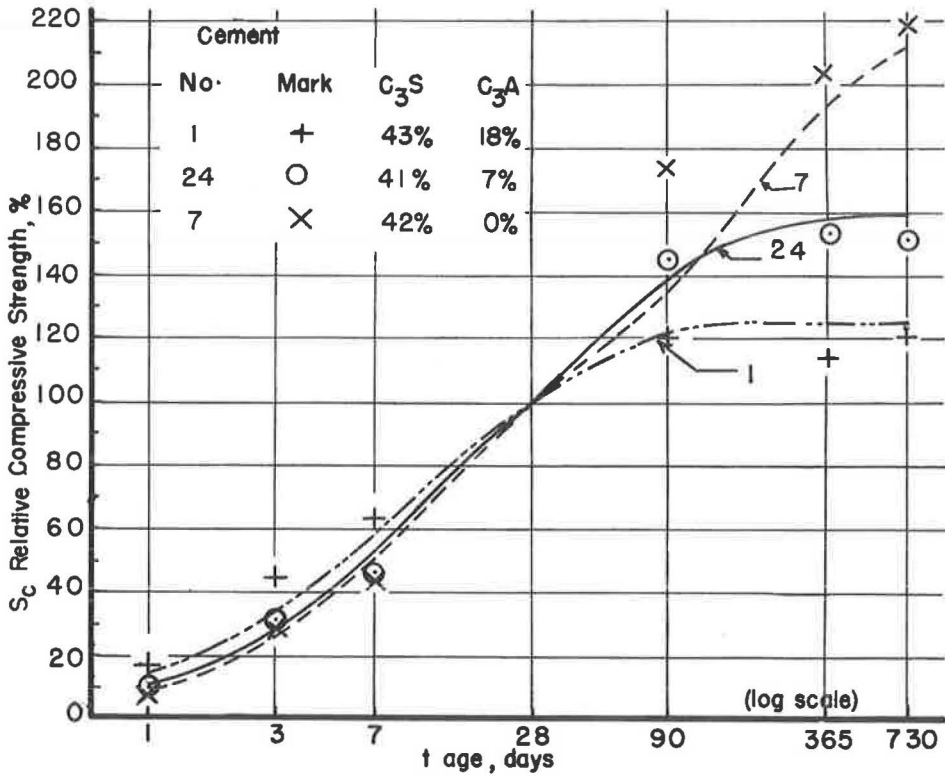


Figure 1. Comparison of experimental and computed values to illustrate effect of C₃A content on the kinetics of the hardening of portland cement in 1:2.75 mortars; experimental values represented by points, computed values by lines.

For the calculation of the factors of p, a₁, and a₂, the potential compound compositions of clinkers were used that were computed by Gonnerman. These factors were substituted into Eq. 6, and the values calculated by a digital computer were compared to Gonnerman's experimental values of relative strength (Table 1).

A group of the calculated values and experimental results is shown in Figure 1. The relative compressive strengths of three cements are plotted from Table 1 as a function of age. The computed C₃S contents of all three cements are practically the same but the C₃A contents are different. Points represent the experimental relative values by Gonnerman, and lines designate the calculated values. The details of the calculations are illustrated in the following.

Example 1. The a parameters of cement No. 1 are calculated by Eqs. 7 and 8:

$$a_1 = 0.22 \text{ and } a_2 = 0.037$$

Substituting these values into Eq. 6:

$$\begin{aligned}
 S_{c,1} &= 100 \frac{1 - 0.43 e^{-0.22t} - 0.57 e^{-0.037t}}{1 - 0.43 e^{-6.15} - 0.57 e^{-1.04}} \\
 &= 100 \left(1.25 - 0.54 e^{-0.22t} - 0.71 e^{-0.037t} \right)
 \end{aligned}$$

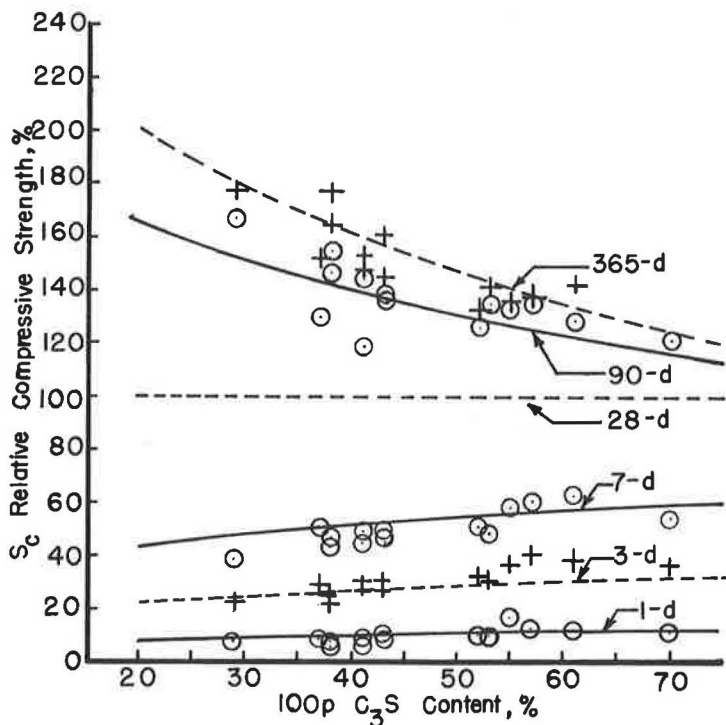


Figure 2. Experimental and computed values for relative compressive strengths of 1:2.75 mortars as a function of the C_3S content for portland cements with computed C_3A content between 5 and 8 percent; experimental values represented by points, computed values by lines.

Similarly, the equations of the curves for relative compressive strength vs age for the cements Nos. 24 and 7, respectively, are

$$S_{c, 24} = 100 \left(1.58 - 0.65e^{-0.147t} - 0.93e^{-0.018t} \right)$$

and

$$S_{c, 7} = 100 \left(2.12 - 0.89e^{-0.10t} - 1.23e^{-0.005t} \right)$$

It is apparent from these equations (or from Fig. 1) how significant the effect of C_3A content is on the strength development. Figure 1 also indicates that a straight line approximates the compressive strength vs age relationship in a semilogarithmic system within the limits of 3 and 90 days. Beyond these age limits, however, this approximation is no longer valid.

Another kind of comparison is shown in Figure 2 between experimental and computed strength values of Table 1. For this comparison, the relative compressive strength values of those portland cements are plotted as a function of C_3S content, the C_3A contents of which are within 5 and 8 percent. Again, points represent the experimental relative values by Gonnerman, and lines designate the values that were calculated by Eqs. 6, 7, and 8 with $C_3A = 6.5$ percent. Figure 2 shows that (a) there is a good correlation between the C_3S content and the relative compressive strength at various ages of cements with approximately the same C_3A contents; and (b) the model provides the relationship with a fair approximation.

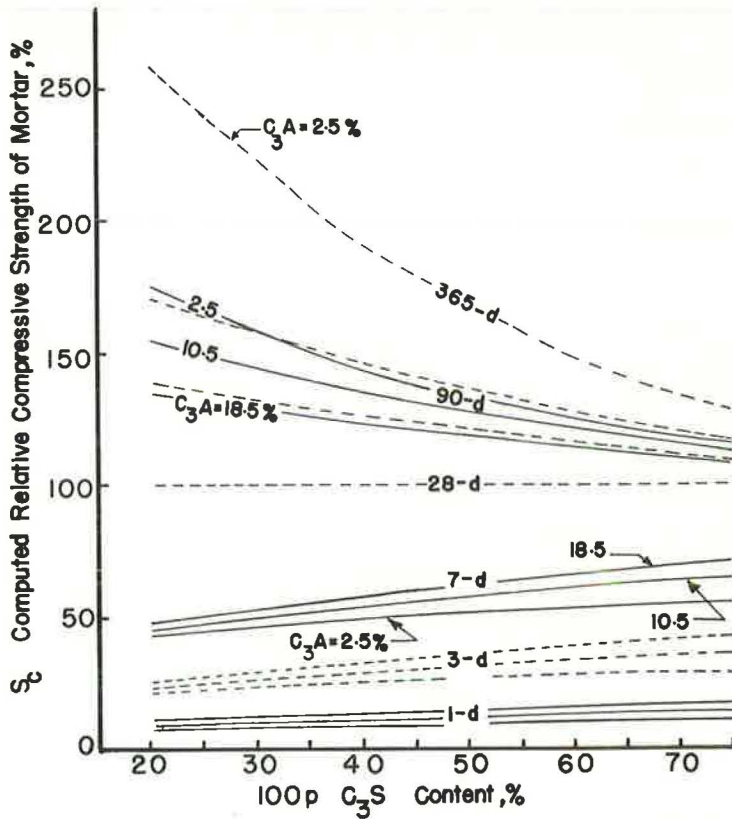


Figure 3. Effect of the C_3A content on the relative compressive strength of 1:2.75 mortars at various ages (computed values).

For other C_3A contents the relationship of strength vs C_3S content will be different, as shown by Figure 3. Relative compressive strength values calculated by Eqs. 6, 7, and 8 are presented as a function of the C_3S content for various C_3A contents and ages. In the families of curves related to the ages of 1, 3, and 7 days, the lower curves, the middle curves and the upper curves represent the C_3A contents of 2.5 percent, 10.5 percent, and 18.5 percent, respectively. This order is reversed in the families of curves related to the ages of 3 months and 1 year. Figure 3 shows that the effect of C_3A on the relative strength of portland cement depends also on the C_3S content, or that the effect of C_3S depends on the C_3A content.

The 410 pairs of strength values in Table 1 show that the agreement between the experimental values by Gonnerman and the calculated values is in most cases acceptable although high discrepancies also exist. The average difference between the experimental and calculated values, computed from the mean square residual, for these results is 11.7 percent; that is, $S_{exp} = S_{cal} \pm 11.7$. Admittedly, some of these discrepancies are due to the applied simplifications in the model. It is also true, however, that the high discrepancies occur mainly with cements that have compositions beyond that of normal portland cements, and/or where they showed retrogression in strength at later ages. For instance, if the 3-month strengths of the cements with 0 percent C_3A content are omitted as well as the 3-month, 1-year and 3-year strengths of the cements Nos. 50 and 51, then the average difference between the experimental and calculated values for the remaining 396 pairs of strength values is reduced to 9.2 percent. The goodness of fit is shown in Figure 4 by plotting these 396 pairs of strength values. The goodness of fit could further be improved by omitting those values from the comparison that show retrogression in strength.

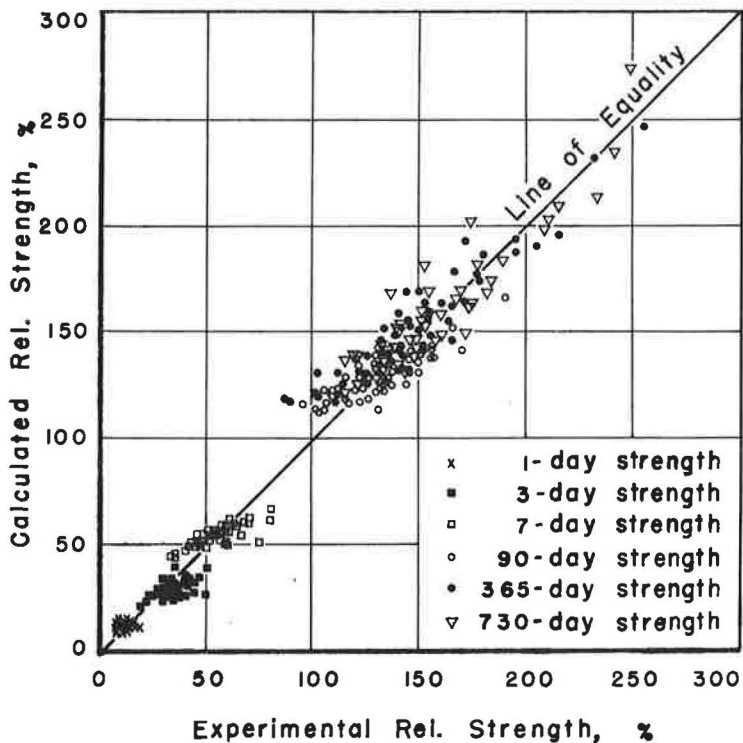


Figure 4. Comparison of 396 experimental values by Gonnerman with computed values of relative compressive strength of 1:2.75 mortars.

TABLE 2
VALUES OF a_1 AND a_2 FOR THE RELATIVE STRENGTH RESULTS BY KIEGER

Type of Test	W/C (by wt)	a_1 , 1/Day	a_2 , 1/Day
Tensile strength of mortar (ASTM C 190-49)		0.80	0.02 C ₃ A
Compressive strength of mortar (ASTM C 109-49)		0.20	0.005 C ₃ A
Flexural strength of mortar		0.45	0.01 C ₃ A
Compressive strength of concrete, 6 bag/cu yd	about 0.43	0.40	0.002 C ₃ A + 0.02
Flexural strength of concrete, 6 bag/cu yd	0.43	0.55	0.001 C ₃ A + 0.02
Compressive strength of concrete, 4½ bag/cu yd	about 0.54	0.30	0.005 C ₃ A
Flexural strength of concrete, 4½ bag/cu yd	0.54	0.5	0.005 C ₃ A
Compressive strength of concrete, 3 bag/cu yd	about 0.80	0.15	0.003 C ₃ A
Flexural strength of concrete, 3 bag/cu yd	0.80	0.25	0.004 C ₃ A

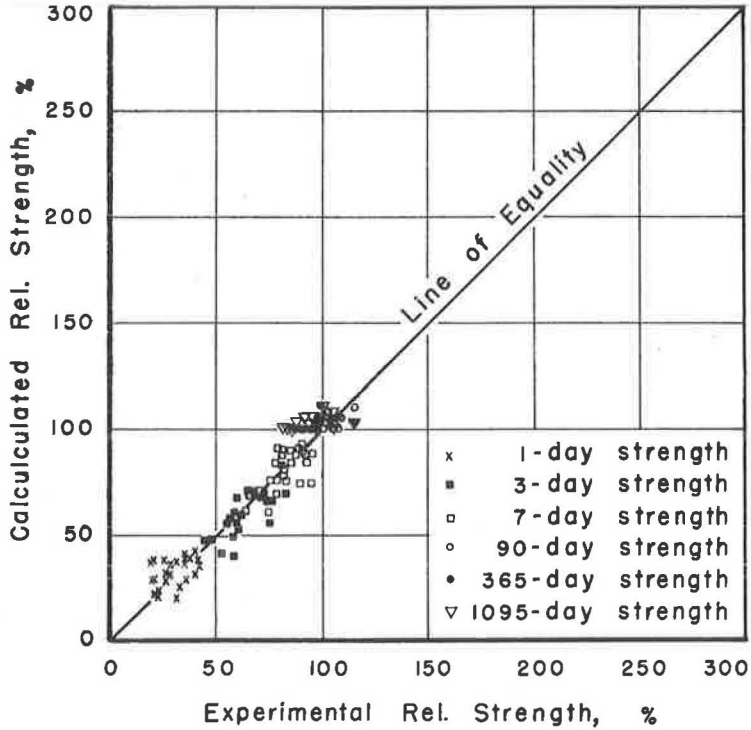


Figure 5. Comparison of 156 experimental values by Klieger with computed values of relative tensile strength of standard 1:3 mortars.

The compressive strengths of the 1:4.25 mortars and the tensile strengths show tendencies similar to the values in Table 1; however, the goodness of fit is poorer between the experimental and calculated values, particularly at the later ages. There are also cements that gave high discrepancies in the 1:2.75 mortar but showed good fit in the 1:4.25 mortar, or vice versa. This seems to indicate that some of the discrepancies are due to the random variation of the experimental results. A non-linear form for Eqs. 7 through 12 might result in a better approximation, but this would again be at the expense of simplicity.

The goodness of fit of the method recommended by Gonnerman for calculation of mortar strength in terms of age and composition of cement was also evaluated. When the calculation was extended to all 410 pairs of strength results, the values calculated by his method provided a somewhat better fit to the compressive strengths of his 1:2.75 standard mortars than the present model did. However, when the comparison was restricted to the 396 pairs of results shown in Figure 4, the goodness of fit was practically the same as that obtained by Gonnerman.

It is important to recognize that Gonnerman needed four empirical constants for each age group in his calculations. Apart from other inconsistencies, this means that his method uses more than 20 empirical constants for the detailed description of the strength development for the period of two years, as compared to the two constants (a_1 and a_2) of the model. Also, the goodness of fit of the model is improved by restricting its use to portland cements of usual composition.

Thus, one can conclude that the experimental results published by Gonnerman (1) verify Eqs. 5 through 12.

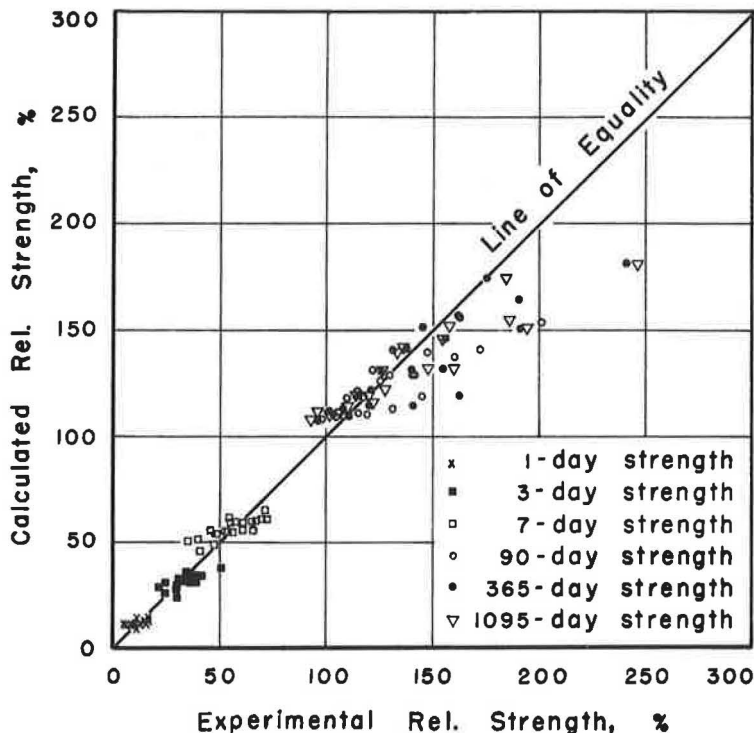


Figure 6. Comparison of 156 experimental values by Klieger with computed values of relative compressive strength of standard 1:2.75 mortars.

Experiments by Woods et al on Mortars

Woods and his co-workers have also published a relevant but short test series for mortar strength (11). The mix proportion of the mortars was 1:3 by weight, both for the compressive and for the tensile strengths. A comparison, the details of which are omitted here, indicated that Eq. 6 provides a reasonable approximation for these mortar strengths, too. More specifically, the same a_1 and a_2 values are suitable for the relative tensile strength here as were presented for the tensile strength results by Gonnerman as Eqs. 11 and 12. However, the following values were found suitable for the relative compressive strength:

$$a_1 = 0.3 \quad (13)$$

$$a_2 = 0.004C_3A + 0.01 \quad (14)$$

These values differ slightly from the values that were recommended as Eqs. 7 through 10, probably due to the difference in the mix proportions of the mortars.

Experiments by Klieger on Mortar and Concrete

Klieger tested the strength of 29 portland cements of different compositions (22). Several of these cements were "treated"; that is, these cements are comparable to the present-day air-entraining cements. The first digit of the cement numbers he used indicates the standard type of the cement. For instance, cement No. 11 is a Type I portland cement.

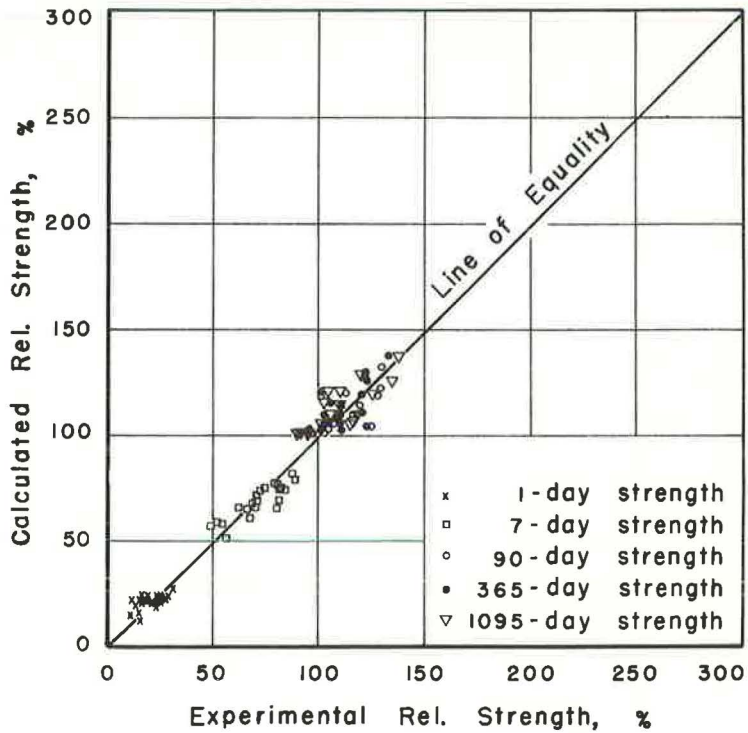


Figure 7. Comparison of 130 experimental values by Klieger with computed values of relative flexural strength of 1:2.75 Ottawa sand mortars.

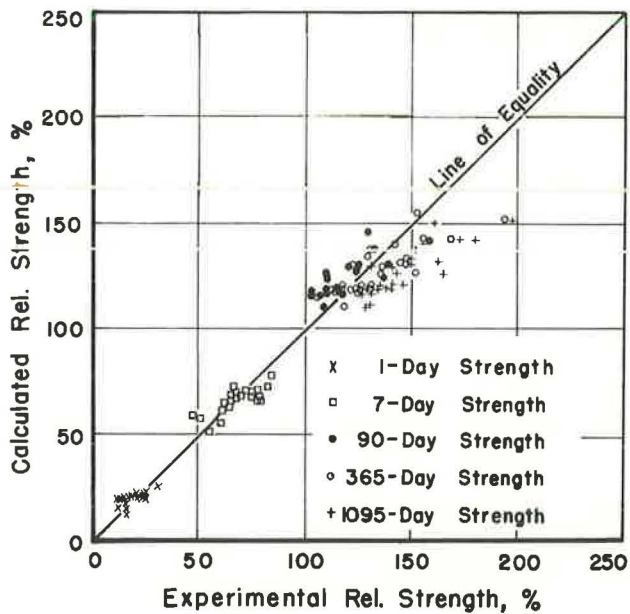


Figure 8. Comparison of the experimental and computed values of relative compressive strength of the 6 bag/cu yd concrete (experimental data by Klieger).

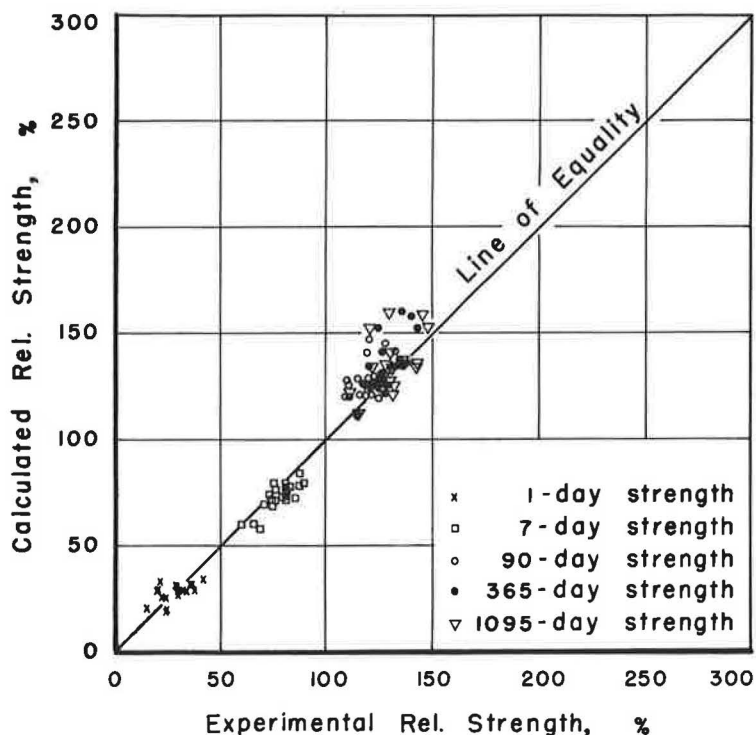


Figure 9. Comparison of 130 experimental values by Klieger with computed values of relative flexural strength of 6 bag/cu yd concretes.

In the mortar series the tensile strength was tested on 1:3 standard Ottawa sand briquets according to ASTM C 190-49; the compressive strength was tested on 1:2.75 graded Ottawa sand plastic cubes (2 in.) according to ASTM C 109-49; and the flexural strength on 1:2.75 graded Ottawa sand plastic prisms. The specimens were cured in moist air at 73 F until test. The characteristics of the tested cements were described by Lerch in a previous paper (23). Accordingly, the SO_3 content of the cements was about 1.6 percent by weight, and the fineness was about 1,800 cm^2/g (Wagner). Only cements Nos. 31, 33, and 33T were exceptions since they had higher fineness and higher SO_3 content. Thus, the hardening of these three cements should be discussed separately.

The compound composition of the cements, calculated again by the Bogue method (21), was also published in Lerch's paper except for cements Nos. 19A, 19B, and 19C, the compositions of which were presented by Klieger. The strength tests were performed at ages of 1, 3, 7, and 28 days, 3 months, 1 and 3 years.

The a values obtained for Klieger's mortar strengths are given in the upper part of Table 2. For usual C_3A contents these values are fairly close to, but not identical with the a values obtained for the Gonnerman mortar tests, probably because of differences in the curing temperature. Thus, values in Table 2 are valid again only under the circumstances that were used by Klieger (limits of C_3A content, fineness, SO_3 content, etc.). Under these circumstances, however, the a values in Table 2 appear suitable for the description of hardening of portland cements in Ottawa sand mortars provided that strengths are determined according to the pertinent standards.

Parenthetically, the value of a_1 for the standard compressive strengths of cements Nos. 31, 33, and 33T is about 0.5 1/day, and the related a_2 is about 0.17 1/day. Although these are only rather rough estimates, comparison with the pertinent values in

TABLE 3
EXPERIMENTAL AND CALCULATED RELATIVE COMPRESSIVE STRENGTHS OF 4½ BAGS PER CUBIC YARD CONCRETES^a

Cement No.	C ₃ S (%)	C ₃ A (%)	Relative Compressive Strength (%)												
			1 Day		3 Day		7 Day		28 Day	3 Month		1 Year		3 Year	
			Exp	Cal	Exp	Cal	Exp	Cal		Exp	Cal	Exp	Cal	Exp	Cal
11	50.0	12.1	13.3	17.5			71.6	67.3	100	108.8	109.9	119.5	110.1	117.9	110.1
11T	51.0	12.2	14.3	17.7			71.8	67.8	100	106.4	109.5	114.2	109.8	121.2	109.8
12	45.0	12.6	10.2	16.6			66.5	65.2	100	116.3	110.2	122.9	110.4	129.1	110.4
12T	46.0	12.5	7.0	16.8			61.0	65.7	100	109.0	110.1	120.0	110.4	125.3	110.4
13	50.0	10.1	18.8	17.6			57.9	66.9	100	121.8	113.3	135.2	113.9	142.5	113.9
14	42.5	8.2	15.4	16.3			67.2	63.2	100	110.0	120.6	126.0	122.3	135.7	112.3
15	64.5	12.1	21.6	20.1			81.1	73.7	100	107.8	106.8	110.3	107.0	109.1	107.0
16	53.5	7.5	17.5	18.6			68.7	68.9	100	112.0	117.6	121.4	119.5	131.1	119.5
16T	52.5	7.9	19.3	18.3			70.8	68.3	100	108.0	117.1	115.0	118.7	132.1	118.7
17	52.0	10.4	12.8	17.9			60.3	67.9	100	111.1	112.1	113.8	112.6	119.3	112.6
18	44.5	13.2	12.0	16.5			64.3	65.3	100	111.2	109.4	116.7	109.6	121.7	109.6
18T	44.0	13.2	9.2	16.4			72.9	65.1	100	105.8	109.4	114.8	109.7	120.3	109.7
19A	36.8	9.8	13.2	15.0			55.2	60.3	100	138.2	118.2	163.2	119.1	191.7	119.1
19B	48.6	9.9	13.1	17.3			62.0	66.2	100	120.5	114.1	127.2	114.8	140.8	114.8
19C	52.0	10.3	16.1	17.9			70.8	67.9	100	112.2	112.3	119.1	112.8	126.2	112.8
21	40.0	6.4	11.7	16.2			56.2	62.4	100	131.3	128.0	160.0	132.5	164.8	132.5
21T	38.0	6.6	9.8	15.7			57.7	61.2	100	128.6	128.4	150.8	132.7	154.3	132.7
22	41.5	6.6	10.9	16.5			54.4	63.2	100	116.5	126.3	128.5	130.3	139.2	130.3
23	51.0	3.7	16.5	19.9			63.9	71.6	100	123.0	128.2	134.7	141.2	141.0	138.3
24	41.0	5.4	15.8	16.9			65.2	63.8	100	124.6	131.2	138.0	138.3	141.0	138.3
25	34.0	4.7	15.5	15.7			49.5	60.5	100	140.8	139.8	164.6	151.9	170.5	151.9
41	20.0	4.5	13.2	12.1			45.6	50.9	100	153.3	155.9	179.7	174.2	177.0	174.3
42	27.0	3.5	14.4	15.0			46.6	58.1	100	185.3	153.6	223.0	180.7	245.3	181.9
43	25.0	6.2	8.9	12.8			46.7	53.4	100	146.0	139.2	177.0	146.0	185.8	146.0
43A	29.0	5.3	13.3	14.2			43.2	56.6	100	165.0	141.2	197.7	151.1	213.9	151.1
51	41.0	3.7	18.5	18.1			61.4	66.5	100	152.3	137.0	162.1	154.1	179.2	154.2

^aThe Exp experimental values were obtained from Klieger's experiments (22); the Cal calculated values were obtained by Eq. 6 with the following factors: $\alpha_1 = 0.30$ and $\alpha_2 = 0.005 C_3A$; T designates cements that are comparable to present-day air-entraining cements.

TABLE 4
EXPERIMENTAL AND CALCULATED RELATIVE FLEXURAL STRENGTHS OF 4½ BAGS PER CUBIC YARD CONCRETES^a

Cement No.	C ₃ S (%)	C ₃ A (%)	Relative Compressive Strength (%)												
			1 Day		3 Day		7 Day		28 Day	3 Month		1 Year		3 Year	
			Exp	Cal	Exp	Cal	Exp	Cal		Exp	Cal	Exp	Cal	Exp	Cal
11	50.0	12.1	31.6	24.9			83.2	72.4	100	113.5	109.9	110.5	110.1	116.8	110.1
11T	51.0	12.2	27.2	25.2			86.4	73.0	100	115.6	109.5	113.5	109.7	115.5	109.7
12	45.0	12.6	14.2	23.3			75.1	69.8	100	111.2	110.2	107.0	110.4	109.1	110.4
12T	46.0	12.5	12.4	23.6			76.7	70.3	100	118.7	110.1	122.5	110.4	117.9	110.4
13	50.0	10.1	27.7	25.2			70.5	72.2	100	118.3	113.2	128.5	113.8	128.5	113.8
14	42.5	8.2	23.8	23.3			77.7	68.0	100	117.3	120.6	121.2	122.3	118.1	122.3
15	64.5	12.1	33.1	29.4			89.2	80.0	100	109.2	106.8	109.2	107.0	102.2	107.0
16	53.5	7.5	25.2	27.2			81.6	74.8	100	116.0	117.5	117.5	119.4	118.2	119.4
16T	52.5	7.9	28.2	26.7			75.4	74.0	100	115.4	117.0	110.0	118.6	120.8	118.6
17	52.0	10.4	18.5	25.8			75.3	73.3	100	113.0	112.1	116.9	112.6	110.8	112.6
18	44.5	13.2	20.0	23.1			78.4	69.8	100	115.3	109.4	113.8	109.6	112.3	109.6
18T	44.0	13.2	17.1	22.9			82.9	69.5	100	121.2	109.5	123.0	109.7	123.0	109.7
19A	36.8	9.8	16.0	20.8			63.9	64.4	100	129.9	118.2	139.3	119.1	149.0	119.1
19B	48.6	9.9	18.1	24.8			71.6	71.4	100	117.2	114.1	125.0	114.8	123.2	114.8
19C	52.0	10.3	25.6	25.8			76.6	73.3	100	116.4	112.3	121.8	112.8	115.0	112.8
21	40.0	6.4	12.7	23.2			64.4	67.3	100	126.2	128.0	139.9	132.4	139.9	132.4
21T	38.0	6.6	15.7	22.5			73.0	65.8	100	121.7	128.4	140.8	132.6	139.0	132.6
22	41.5	6.6	14.8	23.7			66.4	68.1	100	118.7	126.3	118.0	130.2	127.3	130.2
23	51.0	3.7	21.2	29.6			72.3	78.3	100	124.2	128.1	130.0	141.1	124.2	141.2
24	41.0	5.4	22.2	24.5			75.2	69.1	100	118.0	131.1	125.7	138.3	127.3	138.3
25	34.0	4.7	19.3	22.7			59.6	65.3	100	134.0	139.8	144.9	151.9	139.3	151.9
41	20.0	4.5	16.5	16.8			53.0	54.1	100	129.5	155.8	152.0	174.2	145.1	174.2
42	27.0	3.5	19.0	21.5			54.0	62.6	100	165.0	153.6	176.0	180.7	172.0	180.9
43	25.0	6.2	9.8	17.7			52.8	56.7	100	125.1	139.2	125.1	146.0	126.0	146.0
43A	29.0	5.3	15.2	20.0			50.5	60.6	100	141.9	141.2	161.0	151.0	155.1	151.1
51	41.0	3.7	21.0	26.5			63.8	72.4	100	125.1	137.0	131.0	154.1	133.7	154.2

^aThe Exp experimental values were obtained from Klieger's experiments (22); the Cal calculated values were obtained by Eq. 6 with the following factors: $\alpha_1 = 0.50$ and $\alpha_2 = 0.005 C_3A$; T designates cements that are comparable to present-day air-entraining cements.

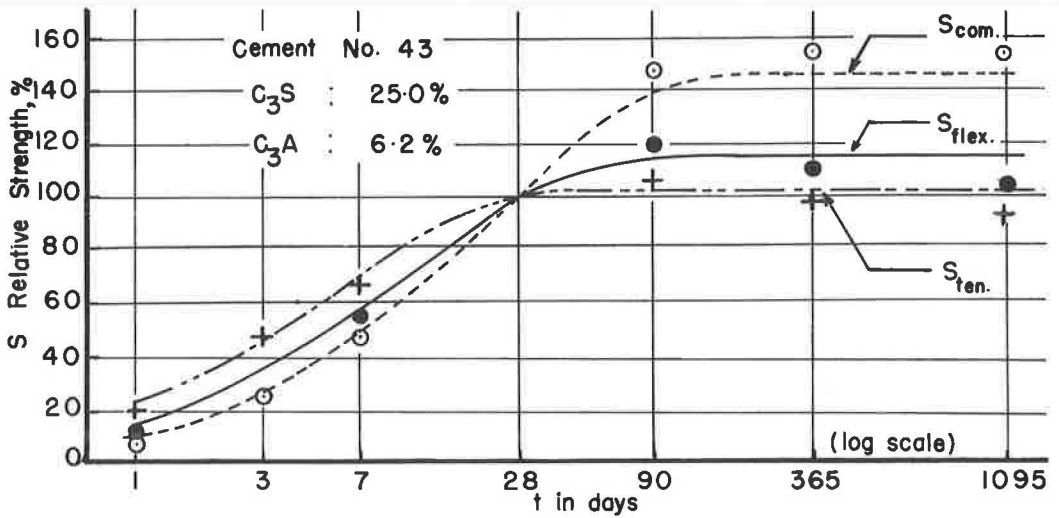


Figure 10. Comparison of experimental and computed values to illustrate effect of test method on the kinetics of the hardening of portland cement in mortars; experimental values represented by points, computed values by lines.

Table 2 shows how conveniently the a parameters can be used for the numerical characterization of the effects on the hardening of portland cements.

The a_1 and a_2 parameters were calculated for each cement with the computed C_3A content by the formulas of Table 2. These factors were substituted into Eq. 6, as in Example 1, and the calculated values were compared to Klieger's experimental values of relative strength as shown in Figures 5 through 7.

Klieger also made two large series of concrete experiments with the same cements with cement factors 6 and $4\frac{1}{2}$ bag/cu yd, respectively, and a short series with 3 bag/cu yd, all with a slump of about $2\frac{1}{2}$ in. Both the compressive strength and the flexural strength of these concretes were measured at ages of 1, 7, and 28 days, 3 months, 1 and 3 years. The flexural strength was determined by third-point loading, and the compressive strength on 6-in. beam ends with the modified cube method according to ASTM C 116-49T. All the specimens were cured continuously moist.

The a values related to these concrete strengths are given in the lower part of Table 2. The values of relative strengths that were calculated by Eq. 6 with the appropriate a_1 and a_2 values are shown in Figures 8 and 9, or for the $4\frac{1}{2}$ bag/cu yd concrete, in Tables 3 and 4, together with the relative strengths obtained from the experimental results by Klieger.

A comparison of the a values for the concretes of two different cement contents reveals that the development of relative strength is quicker and the deceleration is stronger for higher cement contents and for lower water-cement ratios, other factors being equal. Other investigations concerning the relative strength of concrete based on the 28-day strength led to the same conclusion (24, 25, 26).

The calculated values and experimental results are shown in Figure 10. The relative values of tensile strength, compressive strength, and flexural strength of mortars made with the same cement are plotted as a function of age. Points represent the experimental values, and lines designate the values calculated by Eq. 6 with the appropriate values of a_1 and a_2 of Table 2, as shown in Example 1. Again, the rate of increase in the relative tensile strength of a portland cement is much higher than the rate of increase in the relative compressive strength, but the deceleration of the development of tensile strength is also stronger.

Figure 11 shows the relationship at age 7 days between the compressive strength of mortars and the compressive strength of $4\frac{1}{2}$ bag/cu yd concretes (Table 3) made with

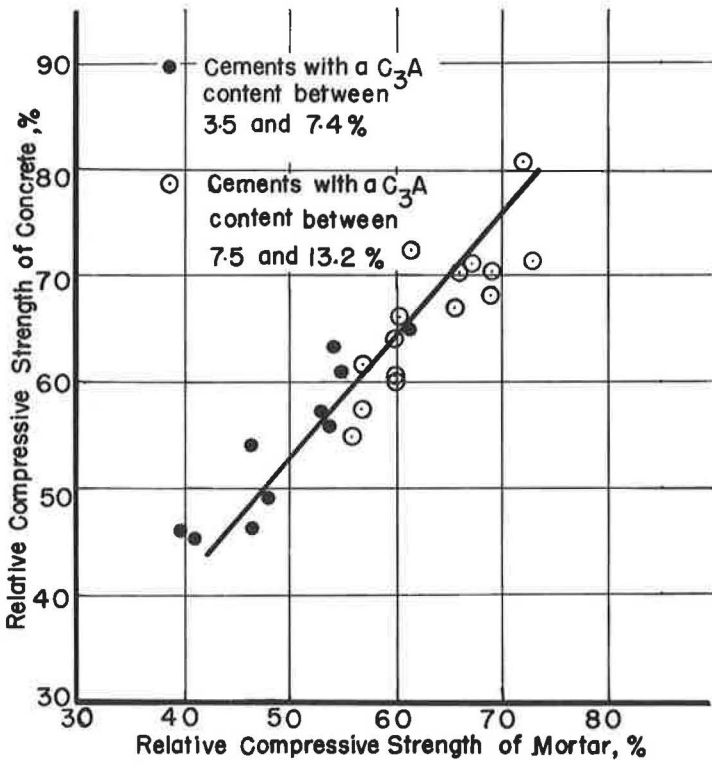


Figure 11. Relationship between the 7-day relative compressive strengths of mortars and $4\frac{1}{2}$ bag/cu yd concretes made with same cements; experimental values represented by points, computed values by line.

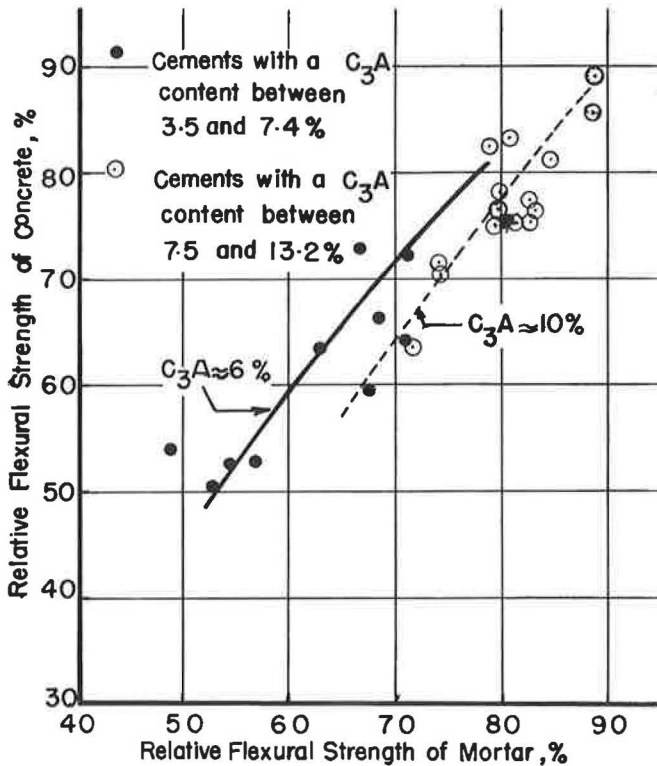


Figure 12. Relationship between the 7-day relative flexural strengths of mortars and $4\frac{1}{2}$ bag/cu yd concretes made with same cements; experimental values represented by points, computed values by line.

TABLE 5
AVERAGE DIFFERENCES BETWEEN EXPERIMENTAL AND CALCULATED
VALUES FOR THE RELATIVE STRENGTH RESULTS BY KIEGER

Type of Test	No. of Exper. Values	Average Difference	Regularity of Differences
Tensile strength of mortar	156	8.2	The calculated values are apt to be slightly high at the age of 3 years.
Compressive strength of mortar	156	13.8	The calculated values for Types 4 and 5 cements are apt to be low at later ages.
Flexural strength of mortar	130	7.1	—
Compressive strength of concrete, 6 bag/cu yd	130	12.5	The calculated values are apt to be low at the age of 3 years.
Flexural strength of concrete, 6 bag/cu yd	130	9.2	The calculated values are apt to be slightly high at later ages.

the same cements. Points represent again the experimental values by Klieger, and the line designates the values that were calculated by Eq. 6 with the appropriate values of a_1 and a_2 . Figure 12 shows the relationship between the 7-day flexural strengths of mortars and $4\frac{1}{2}$ bag/cu yd concretes (Table 4) made with the same cements.

Figures 5 through 9 and Tables 3 and 4 show that there are quite a few discrepancies between the strength values calculated by Eq. 6 and the experimentally obtained values. Nevertheless, the number of serious differences is relatively low compared to the total number of experimental data given here. For the numerical illustration of the overall goodness of fit, Table 5 gives the average values of the differences between the calculated and experimental data shown in Figures 5 through 9. Further analysis reveals that the greater average differences of the compressive strengths are due mainly to the inadequacy of the calculated compressive strengths of the Type 4 and Type 5 portland cements at the ages of 1 and 3 years. Apart from these, however, the obtained overall goodness of fit does not seem inferior to the usual agreement between results of repeated strength tests. Reference is made here to the random variations in Figure 1 of Klieger's paper (22) that compares the experimental results of two tensile strength series made with the same cements.

Figures 11 and 12 provide further indirect verification of the model. They not only show that the experimentally obtained relationship between the flexural strengths of concretes and standard mortars is dependent on the C_3A content of the cement, while the relationship for compressive strength is not, but also that the model is sensitive enough to reflect these phenomena.

Thus, it may be concluded that the experimental data published by Klieger also verify the recommended model for the kinetics of hardening of air-entraining and non-air-entraining portland cements from the age of 1 day to 3 years. Exceptions are the 1-yr and 3-yr compressive strengths of Type 4 and Type 5 portland cements that the model is apt to underestimate. This also means that, within these time limits, the model can be used for the description of the hardening of standard mortar specimens with the values given in the upper part of Table 2, provided that the fineness of the cement is about 1,800 cm^2/g (Wagner), and the SO_3 content is about 1.6 percent by weight.

CLOSING REMARKS

After the completion of the first draft of the manuscript, the author learned that Eqs. 3 and 4 could also have been obtained from the assumption that the hydration of C_3S and the hydration of the second component are so-called "first order reactions." To show this, it is enough to point out that Eq. 3 is also a solution of the following differential equation:

$$\frac{ds_1}{dt} = a_1 (s_0 - s_1) \quad (15)$$

where the symbols are identical with those of Eq. 2. Eq. 15 is the mathematical definition of the term "first order reaction." This also shows that the parameter is the ratio of the rate of hardening and the remaining strength at a given age, and as such is called the "specific reaction rate." Despite the simpler form of Eq. 15, the author kept Eq. 2, alias Condition 4, as the starting point for the development of the model. The main purpose for this was to put emphasis on the concept of deceleration of hardening which, along with the rate of hardening, contributes to a more complete picture concerning the kinetics of hardening of portland cement.

An attempt was also made to use the actual compound composition of cements rather than the potential composition for the calculation of relative strength values by the presented formulas. This was possible because the actual compound compositions of cements used in the discussed experiments of Klieger were determined by microscopic examination (27). However, the strength values calculated with these actual compositions did not show better approximation to the experimental values than when the potential compound composition was used.

Finally, results of preliminary investigations seem to support the applicability of the presented model for the description of the development of heat of hydration as well as for the relation of "maturity" versus strength of portland cement. These results will be presented in another paper.

NEED FOR FURTHER RESEARCH

The presented correlations between the calculated and experimental values are not inferior to the majority of the accepted correlations in concrete technology. On the other hand, the author does not want to give the impression by this that he is completely satisfied with the recommended model as it is, because he is not. This model is only the first step of a new attempt and, as such is necessarily crude. It is believed, however, that this method is applicable for a variety of portland cements in its present form, and seems promising enough to invite further work for the refinement of this model concept, including the development of a theory for the background of the model.

First of all, the approximation of the model for the compressive strength of Type IV and Type V portland cements at later ages is less satisfactory. It is conceivable, of course, that a modification of the model, such as a different interpretation of the factor p , or a different form of parameter a , or a change in the third condition for the model concerning the final strengths of the hardening components, or a consideration of the minor components of cement, etc., would reduce the discrepancies between the experimental results and calculated values. Thus, further research in this direction is desirable.

But besides these, numerous other questions remained open in connection with the model that can be answered only after further successful research. Several items for future research are as follows:

1. Derivation of the form of the parameters as a function of C_3A content from theoretical considerations.
2. Determination of the effects of fineness, temperature, mix proportion, admixtures, etc., on the numerical values of the parameters.
3. Application of the model to further aspects of the kinetics of the hydration of portland cements, such as the nonevaporable water content and specific surface of the cement gel.

4. Investigation concerning the cause of the substantial difference between the kinetics of the development of compressive strength and that of the tensile strength.
5. Application of the model for the strength of high alumina cements.

CONCLUSIONS

1. The extent of agreement between the analyzed experimental results and the values calculated by Eq. 6 is not inferior to the majority of the accepted correlations in concrete technology. Therefore, until a better method is found, it is suggested that the presented simple model is applicable for the kinetics of the hardening of a large group of air-entraining and non-air-entraining portland cements up to the age of three years.

2. The specific rate of strength development of a portland cement can be considered as a linear function and the specific deceleration of the strength development as a quadratic function of the C_3A content of the cement. The effect of the C_3S on the strength depends also on the C_3A content, and vice versa (Fig. 3).

3. The specific rate and deceleration of the strength increase are considerably greater in the case of tensile strength, than in the case of compressive strength (Fig. 10). A further analysis of this phenomenon might contribute to a better understanding of the relationship between the structure of cement paste and its strength.

4. The a_1 parameter characterizes the early strength development, while the a_2 parameter characterizes the strength development at later ages. Thus, the model appears to provide an improved tool for the numerical description of certain effects, such as temperature and admixtures, on the hardening process of portland cements.

5. The recommended model can also describe the relationship between the strengths of mortars and strengths of concretes made with the same cements with a reasonable accuracy (Figs. 11 and 12).

REFERENCES

1. Gonnerman, H. F. Study of Cement Composition in Relation to Strength, Length Changes, Resistance to Sulfate Waters and to Freezing and Thawing, of Mortars and Concrete. *ASTM Proc.*, Vol. 34, Part II, 1934, pp. 244-295.
2. Fontaine, M. Contribution a l'etude de la resistance du beton en fonction de son age (Contribution to the Study of Concrete Strength as a Function of Age). *Rilem Bull.* No. 22, Paris, March 1964, pp. 69-71.
3. Goral, M. L. Empirical Time-Strength Relations of Concrete. *ACI Jour.*, Proc., Vol. 53, Aug. 1956, pp. 215-224.
4. Hald, A. *Statistical Theory With Engineering Applications*. John Wiley & Sons, Inc., New York, 1952, pp. 541-546.
5. Hummel, A. *Das Beton-ABC (Alphabet of Concrete)*, 12th Ed. Verlag von Wilhelm Ernst & Sohn, Berlin, 1959, pp. 115-116.
6. Plowman, J. M. Maturity and the Strength of Concrete. *Mag. of Concrete Res.*, Vol. 9, No. 22, March 1956, pp. 13-22.
7. Duriez, M., and Arrambide, J. *Nouveau traite de materiaux de construction (New Treatise of the Materials of Construction)*. Vol. 1, Dunod, Paris, 1961, pp. 667-685.
8. Brunauer, S., and Kantro, D. L. The Hydration of Tricalcium Silicate and Beta-Dicalcium Silicate From 5° C to 50° C. *The Chemistry of Cements* (H. F. W. Taylor, Ed.), Vol. I, Chap. 7, Academic Press, London & New York, 1964.
9. Copeland, L. E., and Kantro, D. L. Chemistry of Hydration of Portland Cement at Ordinary Temperature. *The Chemistry of Cements* (H. F. W. Taylor, Ed.), Vol. I, Chap. 8, Academic Press, London & New York, 1964.
10. Murphy, G. *Similitude in Engineering*. The Ronald Press, New York, 1950, pp. 57, 71.
11. Woods, H., Starke, H. R., and Steinour, H. H. Effect of Cement Composition on Mortar Strength. *Eng. News-Record*, Vol. 109, No. 15, 1932, pp. 435-437.
12. Bogue, R. M. *The Chemistry of Portland Cement*, 2nd. Ed. Reinhold Publishing Co., New York, 1955, p. 672.

13. Bogue, R. H., and Lerch, W. The Hydration of Portland Cement Compounds. *Industrial and Engineering Chemistry*, Vol. 26, Aug. 1934, p. 837.
14. Lea, F. M., and Desch, C. H. *The Chemistry of Cement and Concrete*, 2nd Ed. Edward Arnold Ltd., London, 1956, p. 81.
15. Venaut, M. *Compte rendu d'un voyage d'etudes aux Etats-Unis et au Canada (Mai 1965) (Report of a Study Tour in the United States and Canada)*. *Revue des Materiaux de Construction, Ciments & Betons*, Oct. and Dec. 1965, Nos. 601 and 603.
16. Verbeck, G. Cement Hydration Reactions at Early Ages. *Jour. PCA R and D Lab.*, Vol. 7, No. 3, Sept. 1965, pp. 57-63.
17. Kesler, C. E., and Ali, Iqbal. Mechanisms of Creep in Concrete. *Symposium on Creep of Concrete*, ACI Publ. SP-9, Detroit, 1964, pp. 35-62.
18. Czernin, W. *Cement Chemistry and Physics for Civil Engineers*. Crosby Lockwood & Son Ltd, London, 1962, Part 3.
19. Ramberg, W., and Osgood, W. R. Description of Stress-Strain Curves by Three Parameters. *NACA*, TN 902, July 1943.
20. Hansen, T. C. Influence of Aggregate and Voids on Modulus of Elasticity of Concrete, Cement Mortar, and Cement Paste. *ACI Jour., Proc.*, Vol. 62, Feb. 1965, pp. 193-216.
21. Bogue, R. H. Calculation of Compounds in Portland Cement. *Industrial and Engineering Chemistry (Analytic Ed.)*, Vol. 1, Oct. 15, 1929, p. 192.
22. Klieger, P. Long-Time Study of Cement Performance in Concrete. Chap. 10, *Progress Report on Strength and Elastic Properties of Concrete*, *ACI Jour., Proc.*, Vol. 54, Dec. 1957, pp. 481-504.
23. Lerch, W. C., and Ford, C. L. Long-Time Study of Cement Performance in Concrete. Chap. 3, *Chemical and Physical Tests of the Cements*, *ACI Jour., Proc.*, Vol. 44, April 1948, pp. 743-795.
24. Jevtic, D. Influence de l'age sur la resistance—Quelques essais effectués avec un ciment a haute resistance initiale (Effect of Age on Strength—Experiments With a High Early Strength Cement). *Rilem Bull.* No. 5, Paris, Dec. 1959, pp. 41-48.
25. Wischers, G. Einfluss der Zusammensetzung des Betons auf seine Fruehfestigkeit (Influence of Concrete Composition on Early Concrete Strength). *Betontechnische Berichte* 1963, *Beton-Verlag GmbH, Duesseldorf*, 1964, pp. 136-151.
26. Ackroyd, L. W., and Rhodes, F. G. An Investigation of the Crushing Strengths of Concrete Made With Three Different Cements in Nigeria. *Proc. Inst. of Civ. Eng.*, Vol. 27, London, Feb. 1964, pp. 325-340.
27. Brown, L. S. Long-Time Study of Cement Performance in Concrete. Chap. 4, *Microscopical Study of Clinkers*, *ACI Jour., Proc.*, Vol. 44, May 1948, pp. 887-921.