(*Paper No. 2149.*)

"On the Rate of Hardening of Cement and Cement Mortars."

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A very large mass of experimental data has now accumulated as to the strength of cements, and especially of Portland cement at various ages after mixing. The mechanical tests carried out in this country by Mr. Grant and others, and abroad in the State laboratories at Berlin and Munich, have thrown a great deal of light on the behaviour of cements, and have led to a great improvement of the manufacture.

So far as tests of cements are intended merely as a check on the manufacturer, they are necessarily carried out in a limited time. Seven-day tests, or at most twenty-eight day tests, are alone possible. But obviously such tests are, to some extent, imperfect for the purpose in view. The engineering value of a cement does not depend on the strength soon after it is mixed, but on the strength which accrues to it after a longer interval of time. Now the results of seven-, or even of seven- and twenty-eight-day tests, leave much uncertainty as to the probable strength of the cement after say six months, or a year. One cement has greater initial strength, another gains strength at a greater rate with lapse of time. To infer the probable engineering value of a cement, both the initial strength and the rate of gaining strength must be considered, and to infer the probable ultimate strength something must be known of the law of increase of strength.

Further than this, even when experiments are made at longer intervals of time, a difficulty arises. Notwithstanding the greatest care in preparation, the briquettes have a considerable variation of strength. Hence a series of experimental results shows discrepancies, and if such results are plotted with the times as abscissas and the strength of the briquettes as ordinates, the result is instead of a fair curve, a broken line, from which it is difficult to draw conclusions. A knowledge of the law of hardening, even of an approximate kind, would enable a fair curve to be drawn through such discrepant observations, and would greatly clear up the meaning of the results.

A rational formula for the strength of cement of different ages is not to be hoped for; but it appeared to the Author, that experiments might furnish a law of an empirical kind simple enough to be easily used, and yet agreeing well enough with a sufficiently wide range of experiments to be relied on within reasonable limits.

Let y be the strength of a cement, or cement mortar, in lbs. per square inch, at an age of x weeks after mixing. From some preliminary tentatives the Author found for the relation between x and y, the expression

$$y = a + bx^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a, b, and n, are empirical constants. In this form the equation would not be very convenient to use, for it would require at least three sets of experiments at three different ages of the test-pieces to determine the three constants; and a still greater number would be required for satisfactory results in consequence of the discrepancies which occur in cement-testing.

It appeared, however, that for any given kind of cement, and any given kind of straining action, n had a constant value. Further, by a modification of the formula, a might always be the strength of the cement at seven days' age. Consequently there would remain only one constant to determine. The formula then is

$$y = a + b\,(x - 1)^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where y is the strength of a cement or mortar, at x weeks after mixing, the initial strength of which at seven days is a lbs. per square inch. The constant n has values which can be assigned beforehand, and only the constant b remains to be determined by experiments on test-pieces more than one week old. It will be seen, hereafter, that though b varies, its variation is not within very wide limits, so that when the characters of cements are better known it may be possible to assign for it a probable value, even if experiments are wanting in any given case.

Now since in this equation a is the initial strength of the cement, and b a constant, varying with the rate of increase of strength with time, the two constants exhibit very clearly the character of a cement. If their values are determined for any given cement, and inserted in the equation, a numerical equation is obtained which may be termed the characteristic equation for the cement.

Tension-Tests of Portland Cement.

To examine the applicability of the formula, let the constants be determined for the series of tests of Portland cement briquettes extending over seven years given in Mr. Grant's first Paper.[1] Mr. Grant's Table gives in each case the mean strength of ten briquettes, $2\frac{1}{4}$ square inches in section. In one series the cement was gauged neat; in another series the cement was mixed with an equal weight of clean Thames sand. Mr. Grant's numbers reduced to lbs. per square inch are as follow:—

Age.	Strength per Square Inch.	
	Neat Cement.	1 Cement + 1 Sand.
7 days	363	157
1 month	415	202
3 months	470	244
6 "	525	285
9 "	542	307
12 "	547	320
2 years	590	351
3 "	585	350

Now for Portland cement in tension $n = \frac{1}{3}$; the constant a has the values 363 and 157 for the two series, and it only remains to determine the most probable value of b in the equation—

$$y = a + b\sqrt[3]{x - 1}$$

This is best done by calculating b for each of the experiments, except that at seven days, and taking the mean of the values so found. Thus—

Neat Cement.

Age. x.	Strength. y.	$y - a$.	$b = \frac{y - a}{\sqrt[3]{x - 1}}$.	Strength. y by Formula.
1	363	..	..	363
4	415	52	36	431
13	470	107	47	471
26	525	162	56	503
39	542	179	53	525
52	547	184	49	541
104	590	227	48	588
156	585	..	..	..
	Mean	. . . .	48	

[1] Minutes of Proceedings Inst. C.E. vol. xxv. p. 89; also vol. xxxii. p. 280.

1 Cement + 1 Sand.

Age. x.	Strength. y.	$y - a$.	$b = \frac{y - a}{\sqrt[3]{x} - 1}$.	Strength. y by Formula.
1	157	..	..	157
4	202	45	31	214
13	244	87	38	249
26	285	128	44	274
39	307	150	45	292
52	320	163	44	305
104	351	194	41	345
156	350	193	36	372
208	363		—	
260	365	Mean . . .	40	

Hence the characteristic equations for this cement and cement mortar are—

Neat cement . . . . . . $y = 363 + 48 \sqrt[3]{x -}$
Cement mortar . . . . . $y = 157 + 40 \sqrt[3]{x - 1}$

Hence the sand reduces the initial strength of the cement by rather more than one-half (from 363 to 157 lbs. per square inch), and the gain of strength at any age is less for the mortar than for the neat cement in the proportion of 40 to 48. By comparing the calculated and observed values of y, it will be seen that the formula agrees closely enough with experiment for practical purposes. Mr. Grant's figures show that the neat cement reached its maximum strength in one hundred and four weeks, and the cement and sand in one hundred and fifty-six weeks. Hence values of b are calculated from data up to those dates only.

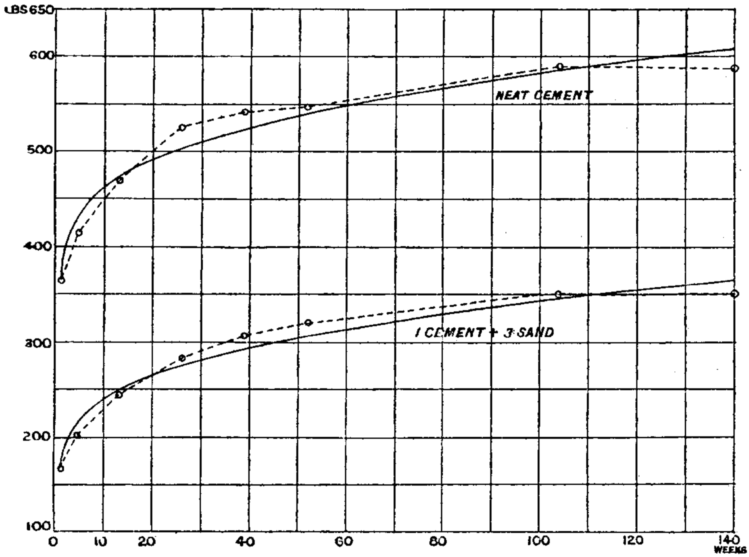
In Fig. 1 the experimental values are shown by small circles, connected by a broken dotted line, and the calculated values lie on the curves.

In the case of cement mortar the briquettes gain in strength up to any period to which experiments are usually extended. But with neat cement briquettes, a maximum strength appears to be reached, often in about three months, after which the strength remains constant or slightly falls off. For example, in the experiments given by Mr. Grant on the relative strength of briquettes made on an impervious slab, and on a porous (gypsum) slab,[1] the strength slightly diminishes after thirteen weeks. Hence

[1] Minutes of Proceedings Inst. C.E. vol. lxii. p. 142.

for such results the value of b must be deduced from experiments before the maximum is reached, and the formula ceases to apply

Fig. 1.



beyond the maximum. The following characteristic equations were deduced for these experiments from the results for four, eight-and-a-half, and thirteen weeks.

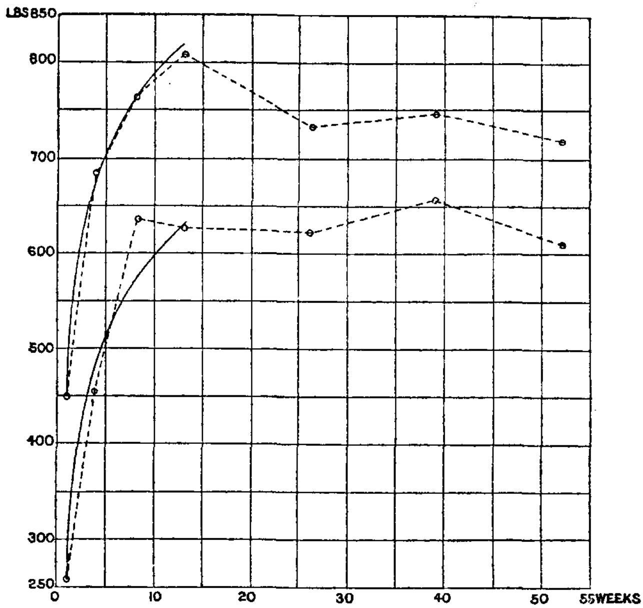
Neat Cement.

Impervious slab . . . . . . $y = 449 + 161\sqrt[3]{x-1}$;
Gypsum slab . . . . . . $y = 257 + 164\sqrt[3]{x-1}$.

x Weeks.	Impervious Base.		Gypsum Slab.	
	y Observed.	y Calculated.	y Observed.	y Calculated.
1·0	449	449	257	257
4·0	687	681	454	493
8·5	765	765	634	577
13·0	808	819	626	631
26·0	731	..	620	..
39·0	746	..	655	..
52·0	718	..	608	..

These results are plotted in Fig. 2. The gypsum-slab results are somewhat irregular, but the theoretical curve strikes a fair balance between the observations.

FIG. 2.



In Table XXX. p. 149, of Mr. Grant's Paper, is given a very complete series of experiments on the effect of fineness of grinding on the strength of briquettes of neat cement, and cement and sand. Part of the briquettes were made with coarsely-ground cement, having 10 per cent. residue on a sieve of 50 meshes, and part of the same cement sifted through a 180-mesh sieve. The experimental results furnish the following equations:

Neat cement, unsifted.

$$y = 353 + 122 \sqrt[3]{x - 1}.$$

The same, sifted.

$$y = 346 + 36 \sqrt[3]{x - 1}$$

Unsifted cement and sand, 1 to 3.

$$y = 75 + 69 \sqrt[3]{x - 1}.$$

Sifted cement and sand, 1 to 3.

$$y = 252 + 53 \sqrt[3]{x - 1}.$$

Unsifted cement and sand, 1 to 5.

$$y = 31 + 46 \sqrt[3]{x - 1}.$$

Sifted cement and sand, 1 to 5.

$$y = 136 + 47 \sqrt[3]{x - 1}.$$

Figs. 3, 4, 5 show these results plotted as before.

Here the reduction of strength by the addition of sand, and the superiority of the sifted cement when mixed with sand are more easily seen in the equations than in Mr. Grant's Table. Further, the exact nature of the effect of sifting the cement can be gathered.

FIG. 3.

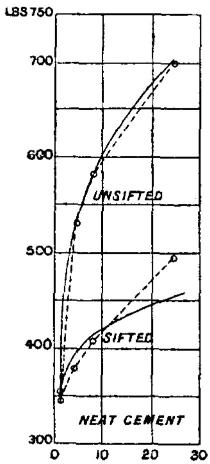


FIG. 4.

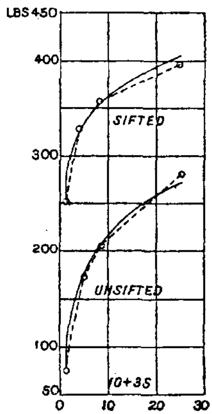
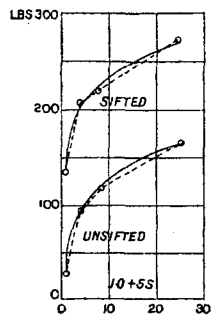


FIG. 5.



With neat cement increased fineness diminishes the gain of strength with age, that is, the constant b diminishes. When mixed with sand, the gain of strength with age is the same whether the cement is sifted or not, but with the sifted cement the initial strength is greater.

The following Table gives the observed strength in lbs. per

Age of Briquette in Weeks. x.	Unsifted Neat.		Sifted Neat.		Unsifted 1 C. + 3 S.		Sifted 1 C. + 3 S.		Unsifted 1 C. + 5 S.		Sifted 1 C. + 5 S.	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1	353	353	346	346	75	75	252	252	31	31	136	136
4	533	529	380	398	171	174	330	328	97	97	208	204
8	585	586	409	415	206	208	358	353	118	119	223	225
25	701	705	495	454	282	273	397	405	166	164	272	271

square inch, and the strength calculated by the equations given above. The agreement is obviously very satisfactorily close.

Again, Mr. Grant gives at p. 143, experiments on the influence of different finenesses of sand on the strength of the cement mortar. In this case, the strength at one week is not stated; but by inversion of the formula it is easily obtained. The characteristic equations are found to be—

1. Sand passing a 20-mesh and retained on a 30-mesh sieve. Pressed—

$$y = 73 + 31 \sqrt[3]{x - 1}.$$

2. The same sand. Ordinary pressure—

$$y = 89 + 19 \sqrt[3]{x - 1}.$$

3. Coarser sand, passing a 10-mesh, and retained on a 20-mesh sieve—

$$y = 172 + 28 \sqrt[3]{x - 1}.$$

The following Table gives the observed and calculated strength:—

Age. Weeks.	(1.)		(2.)		(3.)	
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.
1·0	..	73	..	89	..	172
4·0	117	117	116	116	212	212
8·5	134	134	126	121	237	227
13·0	145	144	124	132	206	236
26·0	156	163	135	144	253	253
39·0	158	177	160	153	268	266
52·0	213	190	182	160	274	279

Here again the discrepancies do not appear greater than the probable errors of the experiments themselves. The differences between successive observed values are not regular as they should be, and in the strength of (3) at thirteen weeks, the observed value must be nearly 40 lbs. too low.

The influence of different proportions of sand on the strength of cement mortar, is shown clearly in the following values of the constants deduced from a very regular and complete series of experiments in the report on the Main Drainage Works at Boston, by Mr. E. C. Clarke. The experiments were extended to a year, and fit the formulas very closely.

Neat cement	$y = 303 + 61 \sqrt[3]{x - 1}$
1 cement + 1 sand	160 + 57
1 cement + 2 sand	126 + 44
1 cement + 3 sand	95 + 36
1 cement + 5 sand	55 + 26

In the same report there are some good experiments on the effect of fineness of grinding of the cement. A cement was sifted through a 120-mesh sieve, and the coarse and fine portions were mixed in different proportions. Briquettes made with three and five parts of sand gave the following results:—

Percentage of Coarse Particles in Cement.	1 Cement + 3 Sand.	1 Cement + 5 Sand.
55	$y = 39 + 28 \sqrt[3]{x-1}$	$y = 19 + 19 \sqrt[3]{x-1}$
33	92 + 42	43 + 32
28	97 + 45	47 + 35
18	117 + 44	65 + 35
8	123 + 50	73 + 36
0	154 + 44	86 + 35

The Author has examined a great number of experiments in this way, and in no case are the discrepancies between the calculated and observed values materially greater than in these Tables. The formula may, therefore, be taken as a sufficiently accurate formula of interpolation. It will be useful next to examine what is the range of value of the constants for different qualities of cements.

Values of Constants for different Cements.

First some data will be selected from the large Table XLVII., p. 169, of Mr. Grant's Paper. The only principle of selection adopted was to take those cements for which the completest series of data are given. The following Table gives the characteristic equations obtained for neat cement briquettes, the constants being in all cases deduced from the strengths given at one, four, and thirteen weeks. In none of these cements did the strength increase beyond that period.

Characteristic Equations for Mr. Grant's Cements.

Units, lbs. per square inch, and weeks. Gauged neat.

No.	Water used per cent.	Setting Time in Minutes.	Characteristic Equation.	Initial Strength.	Strength at 13 weeks.		Strength at 52 weeks.
					Observ.	Calc.	
1	18·5	Slow	$y = 558 + 96 \sqrt[3]{x-1}$	558	815	778	825
12	22·5	15	„ 422 + 118 „	422	744	692	694
13	20·0	600	„ 614 + 91 „	614	846	824	813
„	21·2	„	„ 610 + 91 „	610	840	820	779
„	22·5	„	„ 520 + 112 „	520	783	780	772
15	20·0	480	„ 626 + 56 „	626	824	755	718
„	22·5	„	„ 576 + 140 „	576	833	896	785
19	22·5	„	„ 422 + 188 „	422	793	852	747

The tests of cement which form the most complete series are, however, to be found in the publications of the Engineering Laboratories of Munich and Berlin. In the Mitt. aus den mech. techn. Laboratorium in München, for 1879, there is a remarkable series of experiments on the tensile strength of cements, by Professor Bauschinger. In Table II. are given no less than three hundred and sixty results, each the mean of ten separate experiments. Ten different cements were used, and these were made into test-pieces of 72 square centimetres (11 square inches) section. From these results the Author obtained the following equations, those for neat cements being deduced from results on test-pieces one week to sixteen weeks old, and those for cement and sand from results on test-pieces one week to one hundred and nine weeks old.

The extreme regularity of the constants for a great variety of cements and their limited variation in value is remarkable. The comparatively low initial strength may be partly due to the cement being fresh, partly to the size of the test-pieces.

CHARACTERISTIC EQUATIONS for TENSILE STRENGTH of BAUSCHINGER'S CEMENTS.

Units, lbs. per square inch, and weeks.

Cement Mark.	Setting Time. Minutes.	Neat Cement. $y =$	1 Cement + 3 Sand. $y =$	1 Cement + 5 Sand. $y =$
A	80	$199 + 40\sqrt[3]{x-1}$	$81 + 29\sqrt[3]{x-1}$	$43 + 31\sqrt[3]{x-1}$
B	49	121 + 49	46 + 36	26 + 30
C	195	199 + 95	108 + 40	78 + 37
D	136	199 + 53	53 + 61	37 + 47
E	13	185 + 42	85 + 40	60 + 28
F	416	256 + 37	112 + 41	67 + 38
G	9 to 17	227 + 64	91 + 40	67 + 33
H	14 ,, 26	227 + 36	80 + 46	50 + 36
R	344	299 + 61	136 + 37	105 + 31
T	146	227 + 61	114 + 28	71 + 24
		Mean 54	Mean 40	Mean 33·5

Parts of the same test-pieces were subjected to shearing. The following are equations for a few of them:—

Cement Mark.	Neat Cement. $y =$	1 Cement + 3 Sand. $y =$	1 Cement + 5 Sand. $y =$
A	$270 + 43\sqrt[3]{x-1}$	$112 + 49\sqrt[3]{x-1}$	$60 + 52\sqrt[3]{x-1}$
B	142 + 67	46 + 53	31 + 57
R	412 + 57	185 + 55	131 + 61
T	242 + 92	131 + 43	105 + 44

Here the constants are somewhat higher than for tension; but in other respects are similar.

In the Mitth. aus den kon. techn. Versuchsanstalten zu Berlin for 1885, there is a very extensive series of tests of cement by Dr. Böhme, the test-pieces being the ordinary German standard test-pieces of 5 square centimetres section. The object of the research was to determine the influence of some additions to, or adulterations of, cement on its strength. Hence these results will be useful in showing whether the characteristic equation exhibits clearly the peculiarities of the cement.

The cement mixtures used were:—

A. Pure cement of normal fineness.

B. 9 per cent. of the same cement and 10 per cent. of the finest part of the cement sifted through a 180-mesh sieve.

C. 50 per cent. of cement and 50 per cent. of finest sifted cement.

D. 90 per cent. of cement and 10 per cent. of brickdust.

E. 50 per cent. of cement and 50 per cent. of brickdust.

F. 90 per cent. of cement and 10 per cent. of lime.

G. 50 per cent. of cement and 50 per cent. of lime.

And other mixtures the data for which the Author has not reduced. Each cement mixture was tried gauged neat, and also with 1 to 3 of normal sand. The equations obtained were these:—

Cement Mixture.	Gauged Neat. $y =$	1 Cement mixture + 3 Sand. $y =$
A. 100 cement	$586 + 99\sqrt[3]{x-1}$	$199 + 47\sqrt[3]{x-1}$
B. 90 „ + 10 fine cement	499 + 99	214 + 44
C. 50 „ + 50 „	432 + 112	228 + 51
D. 90 „ + 10 brickdust .	452 + 107	137 + 58
E. 50 „ + 50 „	244 + 114	74 + 53
F. 90 „ + 10 lime . .	514 + 71	155 + 48
G. 50 „ + 50 „ . .	262 + 88	82 + 44

For the briquettes gauged neat, the maximum strength is reached in thirteen weeks or a little more, and the equations do not apply beyond that time. The same is true of the briquettes made with sand in the case of the addition of lime (F and G). The remaining briquettes made with sand gained regularly in strength up to fifty-two weeks. It will be seen that the addition of fine cement reduces the strength in neat cement briquettes, and increases the initial strength without much altering the rate of gain of strength in briquettes made with sand. The brickdust diminishes the initial strength, but increases the rate of gain of strength. The lime diminishes the initial strength, and diminishes the gain of strength.

Compression-Tests of Portland Cement.

It seemed worth while to try if a similar equation would apply equally well in the case of compression-tests. In the Paper by Bauschinger already referred to, there is a series of compression-tests quite as extensive and complete as the series of tension-tests.

The test-pieces were cubes of 144 square centimetres (22·3 square inches or 4·75 inches length of side). Either from the large size of the cubes, or the nature of the stress, or some other cause, it is necessary to take $n = \frac{1}{2}$ in the general equation, instead of one-third its value for tension. With this change, the equation fits the compression results satisfactorily. The equation for compression is therefore—

$$y = c + d \sqrt{x - 1}.$$

where y is the compressive strength in lbs. per square inch at x weeks after mixing.

The equations obtained from Bauschinger's results, are as follow, the equations being all applicable to an age of two years at least.

Cement Mark.	Neat Cement. $y =$	1 Cement + 3 Sand. $y =$	1 Cement + 5 Sand. $y =$
A	$1,877 + 206 \sqrt{x-1}$	$953 + 299 \sqrt{x-1}$	$469 + 299 \sqrt{x-1}$
B	953 + 227	313 + 248	199 + 199
C	1,991 + 490	1,038 + 313	740 + 305
D	1,770 + 327	427 + 412	284 + 313
E	1,592 + 341	668 + 320	356 + 263
F	2,404 + 299	825 + 334	540 + 284
G	1,582 + 270	782 + 270	483 + 249
H	1,436 + 334	711 + 270	341 + 256
R	2,631 + 441	1,507 + 341	995 + 341
T	1,920 + 455	1,024 + 313	626 + 227
	Mean 339	Mean 312	Mean 274

Here the first constant, which can be obtained by tests lasting one week only, varies a good deal: but the second constant has no very great range of variation about its mean values. If the initial strength of the cement is known therefore, the strength at any age up to two years can be inferred with a certain degree of approximation.

OTHER CEMENTS.

Some experiments by Dr. Böhme on hydraulic lime have also been examined.[1] These are not very extensive, and they were carried to an age of thirteen weeks only. However, they agree well with a formula of the same general form with $n = 1$. The equation is therefore—

$$y = a + b(x - 1).$$

The following were deduced from the data—

Tension; 1 lime + 1 sand,

$$y = 20 + 11(x - 1).$$

Tension; 1 lime + 3 sand,

$$y = 31 + 17(x - 1).$$

Compression; 1 lime + 1 sand,

$$y = 97 + 44(x - 1).$$

Compression; 1 lime + 3 sand,

$$y = 122 + 22(x - 1).$$

The Paper is accompanied by several diagrams, from which the Figs. in the text have been engraved.

[1] "Mittheilungen aus den k. technischen Versuchsanstalten zu Berlin," 1884, p. 46.