

(*Students' Paper No. 404.*)

"The Effects of Frost on the Strength of Portland Cement."¹

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THE experiments described in this Paper were carried out at the cold-air stores of the Manchester Corporation, with cement which had given the most satisfactory and consistent results in tests made periodically in connection with the work for which it was used. Its mean initial set of 30 minutes and permanent set of 2 hours 10 minutes in a room kept at a temperature of 60° F. are satisfactory, while its mean tensile strength, after setting for 6 hours in air at the same temperature and subsequent immersion in water for 6 days, 14 days, and 28 days, was 440 lbs., 504 lbs., and 513 lbs. per square inch respectively. The residue on a sieve having 75 meshes per lineal inch (5,625 meshes per square inch) averaged $5\frac{1}{4}$ per cent. by weight. Mixed with two parts by measure of sand, its mean strength at 1 month was 159 lbs., and at 2 months 200 lbs. per square inch. On being exposed for 1 hour to moist air at a temperature of 100° F., and subsequently immersed in water at 110° F. for 48 hours, it showed no signs of "blowing." Its weight per bushel was 115 lbs., or 97 lbs. per cubic foot, and its specific gravity 3.12. The particular sample under consideration was taken at random from a large consignment, and the initial set in a room at 60° F. took place at 45 minutes, and the permanent set at 3 hours. Its tensile strength was $553\frac{1}{2}$ lbs., 632 lbs., and 747 lbs. per square inch at 6 days, 14 days, and 28 days respectively. The residue of 3 per cent. by weight on a 75-mesh sieve shows it to have been ground extremely fine.

¹ This Paper was read and discussed at the meeting of the Manchester Association of Students on the 10th March, 1897.

The chemical analysis was as follows:—

		Average Composition of Good Cement.
Silica	23·20	23·32
Sand	0·55	..
Lime (CaO)	58·91	61·56
Magnesia (MgO)	0·68	1·07
Iron oxide (Fe ₂ O ₃)	4·20	12·13
Alumina (Al ₂ O ₃)	8·90	
Sulphuric acid (SO ₃)	1·40	1·28
Loss on ignition (water and carbonic acid)	1·70	0·30
Alkaline oxides (by diff.)	0·46	0·34
	<u>100·00</u>	<u>100·00</u>

A sample was tested by allowing it to set for 3 days and 6 days in a room at 60° F., and it is to these tests that results obtained from the other experiments will be referred and compared. The mean tensile strength of three briquettes so tested after 3 days was 246 lbs., and after 6 days 306 lbs. per square-inch, showing an increase of 24 per cent.

Experiment No. 1.—Rooms at temperatures of 32°, 29°, 25°, 18°, 15°, and 10° F. being available, six briquettes were mixed in each with 22½ per cent. by weight of water, which had been kept in those temperatures for a few minutes and kept moving to prevent freezing. The cement was mixed by being rapidly agitated in an Adies mixer, subsequently turned over with a trowel on a slate slab, and placed in the brass moulds on brass plates as quickly as possible. Little or no difficulty was experienced in working it at the first three temperatures, but at temperatures below 18° F. it was found that the surplus cement from the mixing became stiff, whether from setting or freezing will be discussed later. A small pat of the cement in each case was spread about ¼ inch thick on a small glass plate.

After 3 hours all the briquettes were examined. Those in temperatures of 10° and 15° F. were quite hard, and “frost flowers” appeared in various forms on the surfaces, though there was no actual crystallization on the cement itself. At 18° F. the briquettes had become fairly hard, and refused the impression of the thumb-nail, though not to such an extent as those at 10° and 15° F. Above these temperatures the cement varied from being stiff at 25° F. to being perfectly plastic at 32° F., where moisture was still standing in the moulds.

The results of examination 24 hours after mixing, were: at 32° F. the sample was hard, and a chip broken from the pat, when breathed

on and kept in the warm hand, became plastic but not granular. At 29° F. the sample was hard, and a chip, as before, crumbled in a few moments when held in the hand, and became a moist powder which could easily be worked up to a pasty consistency. At 25° F. the sample was hard, and when warmed in the hand and breathed on became brittle, and was easily pulverized with the fingers, but apparently little moisture remained. At 18° F. the symptoms were similar, but more moisture appeared to remain. At 15° and 10° F. the briquettes were very hard, and a chip from each pat, when pulverized, seemed damp.

After 3 days in these temperatures, three of each batch of briquettes were tested in the cold rooms, to prevent reaction taking place. The moulds in all cases adhered tightly to the brass plates, and at the lowest temperatures were only detachable by sharp strokes on the plate with a mallet; thus removed from the moulds the briquettes were perfect in form, all angles and corners being sharp and well defined (due no doubt to the pores being filled with moisture), and no cement was left on the moulds or plates where it had been in contact. The briquettes from the three higher temperatures were, however, very indifferent, those from 32° F. being somewhat stratified, and a skin of a very brittle character and light grey colour was formed for about $\frac{1}{16}$ inch on the surface of each, and was easily scaled off after the briquettes had been broken. The briquettes were tested to fracture in a Bailey compound lever shot-filling machine, the load being applied at the rate of 100 lbs. in 10 seconds, and the mean tensile strengths of the three briquettes from each temperature were as shown in Table I.

TABLE I.

Cement frozen for 3 days at . . .	32° F.	29° F.	25° F.	18° F.	15° F.	10° F.
Tensile strength in lbs. per square inch	190	189	108 $\frac{1}{2}$	139 $\frac{3}{4}$	203 $\frac{1}{2}$	279 $\frac{3}{4}$

The fracture surface in the first three cases was fairly smooth, and differed little from that of an ordinary test, but the three latter were very granular.

Experiment No. 2.—The three briquettes which had been exposed to each of the temperatures mentioned for 3 days were removed to a room at 60° F. No external change was visible, except that the frozen moisture in the pores on the surface disappeared, and the briquettes became much drier and consequently lighter in colour.

After being allowed to thaw thus for 3 days they were tested, with the results shown in Table II.

TABLE II.

Cement thawed for 3 days at 60° F. after freezing for 3 days at	32° F.	25° F.	25° F.	18° F.	15° F.	10° F.
Tensile strength in lbs. per square inch. . }	382	194	142½	263½	232½	147½
Difference in strength as result of thaw . }	+ 101 per cent.	+ 3 per cent.	+ 31 per cent.	+ 89 per cent.	+ 14 per cent.	- 47 per cent.

On examining the fractured briquettes from this experiment it was found that the specimens varied widely in texture. The briquettes having the smoothest fracture surface gave the highest tensile strength, and the strength decreased as the grain became coarser. It therefore appears improbable that the cement of a texture such as that frozen at 25° F. would ever regain its full strength.

Experiment No. 3.—Briquettes were mixed at a temperature of 40° F., and three were placed in a room at 19° F. immediately, three after 5 minutes, three at 10 minutes, and at various intervals up to 1 hour after mixing, and were exposed to this temperature for 3 days, removed to a room at 60° F., and allowed to thaw for another 3 days, the tensile strengths given after that time being shown in Table III.

TABLE III.—TENSILE STRENGTH IN LBS. PER SQUARE INCH.

Periods for which briquettes were allowed to set before being ex- posed to frost	—	5 Mins.	10 Mins.	15 Mins.	20 Mins.	30 Mins.	1 Hour.
Exposed to temperature 19° F. for 3 days, and subsequently to air at temperature 60° F. for 3 days	90½	118	138	157	167½	195	248½
Cement frozen at 19° F. for 3 days, broken up and ground to pass sieve 20, re-mixed with warm water, and subsequently immersed in water for 6 days.	112½	123½	94½	93½	95½	97½	120
Setting power remaining. .	Per Cent. 2)125	Per Cent. 105	Per Cent. 68½	Per Cent. 59	Per Cent. 57	Per Cent. 50	Per Cent. 48
	62½	52½	34½	29½	28½	25	24

The fracture surfaces in this experiment also varied in texture as in experiment No. 2, and the same remark as to decrease of strength as the grain became coarser holds good in this case also, though perhaps not to such a marked extent.

It might almost be taken as a hypothesis that frost would do the most harm to unset cement, and that frost had less and less effect on the strength as the time which it had been allowed to set before freezing increased, until probably a point would be ascertainable when any consequent decrease in strength would be imperceptible. From this it may be reasonably inferred (1) that more harm would result to a slow-setting cement than to a quick-setting one; (2) that, as the speed of mortar setting varies with the admixture of sand, more harm from frost may be expected.

Experiment No. 4.—To ascertain the accuracy of the statement that though Portland cement from its rapid set would often resist a frost which would affect lime mortar, yet when once the partial set of Portland cement was disturbed it would not again unite, but remain permanently in a pulverulent condition, the Author pulverized cement which had been mixed with water and placed in a room at 10° F. for 3 days, passed the powder so obtained through a sieve with 400 meshes per square inch, and again mixed it into a paste with the addition of warm water. The briquettes so made set quite hard both under water and in air at 60° F., and after 3 days developed a tensile strength of 120 lbs. and 100 lbs. respectively. A similar procedure was followed with cement which had been frozen under the same conditions and subsequently thawed for 3 days at 60° F., but though a slight cohesion was perceptible, it crumbled to a powder, and appeared to have lost all its cementing properties.

Cement mixed at the same time and under precisely the same conditions as briquettes in experiment No. 3, was pulverized, re-mixed with warm water, and allowed to set for 6 days at 60° F. The results obtained are given in Table III.

The last line in the Table gives the percentage of suspended setting power¹ as compared with that expended. As the setting takes place before exposure to frost, the suspension of setting power decreases.² This only applies to the temperature given, viz., 19° F.,

¹ This term is used to express suspended chemical action capable of producing tensile strength.

² The comparison here made of expended power after a subsequent thaw is deemed preferable to comparison to expended power after 3 days' frost only, because in the latter case a correction would have to be made for the tensile strength of ice.

and the proportion of suspended setting power would probably increase conversely as the temperature.

It appears from this experiment that frost attacking a cement will suspend a greater percentage of the chemical action if it is brought to bear soon after mixing, and that the percentage of such suspension will decrease as the opportunity for original setting is curtailed, but it has yet to be proved to what period of exposure to frost, if any limit of time were ascertainable, this statement would cease to be true.

In connection with the foregoing experiment samples of cement were weighed to ascertain the quantity of moisture remaining after various intervals.

(1) 50·4273 grams of cement were mixed with 12·6068 grams of water at a temperature of 43° F., placed on a balance, and the diminution of weight was noted at various intervals up to 3½ hours. The evaporation was greatest at commencement, and gradually decreased (Table IV). A slight correction should be

TABLE IV.

After—	Weight.	Percentage of loss of total water contained in sample.
	Grams.	
—	63·0341	0·000
5 minutes	63·0030	0·404
10 „	62·9720	0·807
15 „	62·9475	1·125
20 „	62·9252	1·415
25 „	62·9085	1·631
30 „	62·8949	1·808
35 „	62·8820	1·976
1 hour	62·8440	2·469
1½ „	62·8145	2·852
2 hours	62·7930	3·032
2½ „	62·7783	3·323
3 „	62·7620	3·535
3½ „	62·7480	3·717
7 days at 212° F. . . .	56·5620	—

made to allow for the weight of carbonic acid absorbed from the atmosphere.

Experiment No. 6.—A sample of cement was mixed and allowed to set for 6 hours in air and 6 days under water at 40° F. It was then suspended by a fine wire and allowed to dry, with a result that the percentage of total moisture available decreased, as shown in Table V.¹

¹ In experiments Nos. 5 and 6, by “the total moisture available,” is meant the amount driven off by continuous heating at 212° F.

It appears that in freshly-mixed cement and that which has been kept moist for some time the moisture is given off in a widely different manner, at any rate at the commencement, the former giving off its moisture at a rate decreasing with time, while the latter allows its moisture to evaporate at a fairly uniform rate for a much longer time.

The following three samples of cement were examined with a

TABLE V.

After—	Weight (gross).	Moisture remaining.	Percentage of total moisture remaining.
	Grams.	Grams.	
1 hour	152·3300	18·7840	100·000
2 hours	152·2400	18·6940	99·521
3 "	152·1180	18·5720	98·871
4 "	152·0153	18·4693	98·324
5 "	151·9204	18·3754	97·831
6 "	151·8250	18·2800	97·311
7 "	151·7270	18·1920	96·848
8 "	151·6164	18·0814	96·260
9 "	151·5255	17·9905	95·775
10 "	151·3600	17·8250	94·895
11 "	151·2269	17·6919	94·185
12 "	151·0900	17·5550	93·457
13 "	151·0312	17·4962	93·144
14 "	150·8658	17·3308	92·263
15 "	150·7528	17·2178	91·662
16 "	150·6100	17·0750	90·900
17 "	150·4764	16·9414	90·190
18 "	150·3521	16·8171	89·534
19 "	150·2269	16·7019	88·915
20 "	150·0492	16·5242	87·969
Heated at 212° F. for 7 days	149·8464	16·3214	86·889
	133·5460	—	—

view of determining whether any chemical difference could be detected in them 6 weeks after mixing:—

- (1) Set in air at 60° F.
- (2) Mixed and set in air at 25° F. for 3 days. Thawed in air at 60° F.
- (3) Mixed and frozen at 10° F. for 3 days, and re-mixed at 60° F.

On scraping portions from the samples for analysis it was found that (1) was hard, (2) medium hard, and (3) soft.

On treating with an alcoholic solution of ammonium chloride, the largest amount of residue was obtained in the case of (2), indicating that least chemical change had taken place in this case. The differences observed were not very striking, however. It must be borne in mind that the hardening of cement is a

mechanical as well as a chemical process. It is probable from experiments which have been made¹ that the chemical change is confined to a small fraction only of the mass, and serves chiefly to bind together the particles cohering to make up the main body of the cement. Any cause tending to destroy the intimate cohering of these particles would be a source of weakness. Thus in the case of (2) the freezing, and in the case of (3) the probably imperfect grinding and re-mixing of the cement, would chiefly account for the loss of strength.

The thermometric readings at the Greenwich Observatory for the ten winters from 1886-87 to 1895-96 inclusive show that frost occurred on 595 days, the greatest consecutive number of such days being 30 in 1894-95. On 73 days the maximum temperature did not attain freezing-point during a maximum of 10 consecutive days in 1890-91. The temperature fell below 15° F. on 9 days, the maximum reading in only one case exceeding 32° F. It cannot therefore be said that the most severe of the Author's tests are beyond the conditions which may reasonably be expected to occur in England; on the contrary, many works would be situated so as to be exposed to much colder winters than would at the same time be experienced at Greenwich, on account of their latitude and proximity to sea-level.

Conclusions.—As a result of the investigations the Author is led to suggest that the following statements may be accepted until more extensive inquiries and experiments are made:—

That frost has a deleterious effect on Portland cement.

That though cement may immediately after frost appear to be seriously damaged it will improve with time, though it is not probable that it would ever regain its original strength.

That frost only partially suspends chemical action in the setting of cement.

That the strength of cement may be expected to suffer most if frozen immediately or soon after mixing, but that the ill effects will be diminished with the amount of set previously attained.

That liability to damage by frost decreases with the amount of water remaining in the cement.

That a relation exists between the original tensile strength and the amount of suspended chemical action capable of producing tensile strength.

Suggestions as to how the best results may be obtained are not wanting, but in most cases lack confirmation. The admixture of

¹ Michel, *Journal für praktische Chemie*, No. 33, 1886, p. 548.

common salt is most favoured. There is a great want of agreement among English authorities on this point though the experience of American engineers shows a strong case in favour of its use. The American practice is to dissolve 1 lb. of salt in 18 gallons of water when the temperature is 32° F., and to add 3 ounces for every 3° of lower temperature. Alum, sugar, caustic potash, soda, or strontia would all probably have a tendency to preserve chemical action.

Cement which under ordinary conditions would be considered too fresh would from its rapid set and development of warmth probably better evade any action of frost. The Author recently tested a sample of cement which, when mixed with water at its own temperature, rose from 62° F. to 82° F. in 5 minutes; but, though it proved perfectly sound in the hot bath and tensile tests, its use is not to be recommended.

The use of warm water instead of cold has much to recommend it, and experiments show that a better result is obtained; but the extra cost would in many cases be a detriment to its use, as also the warming of sand and other materials. It is probable also that a mortar having a fine matrix, or, in other words, very minute pores, would better resist frost than one mixed with very coarse sand. This would be best supplied by smiths' ashes finely ground, which also have the advantage of being vesicular.

In winter all exposed surfaces of work should be protected, and straw, felt, bags of sawdust, or even boards are commonly used; but hurdles thatched with straw are the most effective, as, in addition to not being easily penetrated by frost, they have the advantage of keeping the straw or other material from actual contact with the unset work.

The Author has made no experiments on the effects of frost on lime, but it seems to be agreed that work executed with it would be seriously injured. In Norway, unslaked lime is used for mortar, which is prepared in small quantities as required, and the unslaked lime is increased as the thermometer falls. The theory is that the mortar sets before it cools, for, of course, the quicker the mortar sets the less risk of damage resulting. The degree of frost in which bricklayers may work is variously estimated at between $18\frac{1}{2}^{\circ}$ F. to 14° F. and to 5° above and $1\frac{3}{4}^{\circ}$ below zero F. As a confirmation of this Mr. T. Michell, British Consul-General at Christiania, gives, as an example, that five courses of a wall laid on the 10th March in $1\frac{3}{4}^{\circ}$ F. had to be pulled down on the 12th and 13th March, 1888, owing to a mistake made by the contractor, and that the mortar when attacked with crowbars

proved to be harder than the bricks, the fractures having in many cases run across the bricks instead of following the mortar joints. This is worthy of the consideration of those who have contracts involving the use of lime mortar to execute during frosty weather.

The Author is indebted to the Lord Mayor of Manchester and to the City Surveyor, Mr. T. de Courcy Meade, M. Inst. C.E., for facilities in carrying out the experiments; and wishes to take this opportunity of thanking Mr. Gilbert J. Fowler, M.Sc., for his guidance and assistance in preparing the Paper.

The Paper is accompanied by photographs of the specimens of cements under the various conditions described.