STANDARD SPECIFICATIONS

AND UNIFORM METHODS OF TESTING AND ANALYSIS FOR

Portland Cement

UNIVERSAL
PORTLAND CEMENT CO.
CHICAGO—PITTSBURG

Universal Portland Cement Co

Standard Specifications

and

Uniform Methods of Testing and Analysis

for

Portland Cement

Embracing the Report of the Committee on Standard Specifications for
Cement of the American Society for Testing Materials; the Report of the
Committee on Uniform Tests of Cement of the American Society
of Civil Engineers; and the Report of the Committee on
Uniformity in Technical Analysis for Limestones, Raw
Mixtures and Portland Cements of the Society for
Chemical Industry, (New York Section).

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Standard Specifications for Portland Cement

Adopted by the American Society for Testing Materials,
August 16th, 1909

GENERAL OBSERVATIONS.

These remarks have been prepared with a view of pointing out the pertinent features of the various requirements and the precautions to be observed in the interpretation of the results of the tests.

The Committee would suggest that the acceptance or rejection under these specifications be based on tests made by an experienced person having the proper means for making the tests.

SPECIFIC GRAVITY.

Specific gravity is useful in detecting adulteration. The results of tests of specific gravity are not necessarily conclusive as an indication of the quality of a cement, but when in combination with the results of other tests may afford valuable indications.

FINENESS.

The sieves should be kept thoroughly dry.

TIME OF SETTING.

Great care should be exercised to maintain the test pieces under as uniform conditions as possible. A sudden change or wide range of temperature in the room in which the tests are made, a very dry or humid atmosphere, and other irregularities vitally affect the rate of setting.

CONSTANCY OF VOLUME.

The tests for constancy of volume are divided into two classes, the first normal, the second accelerated. The latter should be regarded as a precautionary test only, and not infallible. So many conditions enter into the making and interpreting of it that it should be used with extreme care.

In making the pats the greatest care should be exercised to avoid initial strains due to molding or to too rapid drying-out during the first twenty-four hours. The pats should be preserved under the most uniform conditions possible, and rapid changes of temperature should be avoided.

The failure to meet the requirements of the accelerated tests need not be sufficient cause for rejection. The cement may, however, be held for twenty-eight days, and a retest made at the end of that period, using a new sample. Failure to meet the requirements at this time should be considered sufficient cause for rejection, although in the present state of our knowledge it cannot be said that such failure necessarily indicates unsoundness, nor can the cement be considered entirely satisfactory simply because it passes the tests.

SPECIFICATIONS.

GENERAL CONDITIONS.

All cement shall be inspected.

Cement may be inspected either at the place of manufacture or on the work.

In order to allow ample time for inspecting and testing, the cement should be stored in a suitable weather-tight building having the floor properly blocked or raised from the ground.

The cement shall be stored in such a manner as to permit easy access for proper inspection and identification of each shipment.

Every facility shall be provided by the contractor and a period of at least twelve days allowed for the inspection and necessary tests.

Cement shall be delivered in suitable packages with the brand and name of manufacturer plainly marked thereon.

A bag of cement shall contain 94 pounds of cement net. Each barrel of Portland cement shall contain 4 bags, and each barrel of natural cement shall contain 3 bags of the above net weight.

Cement failing to meet the seven-day requirements may be held awaiting the results of the twenty-eight day tests before rejection.

All tests shall be made in accordance with the methods proposed by the Committee on Uniform Tests of Cement of the American Society of Civil Engineers, presented to the Society, January 21, 1903, and amended January 20, 1904, and January 15, 1908, with all subsequent amendments thereto.

The acceptance or rejection shall be based on the following requirements:

PORTLAND CEMENT.

DEFINITION.—This term is applied to the finely pulverized product resulting from the calcination to incipient fusion of an intimate mixture of properly proportioned argillaceous and calcareous materials, and to which no addition greater than 3% has been made subsequent to calcination.

SPECIFIC GRAVITY.

The specific gravity of cement shall not be less than 3.10. Should the test of cement as received fall below this requirement, a second test may be made upon a sample ignited at a low red heat. The loss in weight of the ignited cement shall not exceed 4 per cent.

FINENESS.

It shall leave by weight a residue of not more than 8% on the No. 100, and not more than 25% on the No. 200 sieve.

TIME OF SETTING.

It shall not develop initial set in less than thirty minutes; and must develop hard set in not less than one hour, nor more than ten hours.

TENSILE STRENGTH.

The minimum requirements for tensile strength for briquettes one square inch in cross section shall be as follows and the cement shall show no retrogression in strength within the periods specified:

Age.	*Strength.*
Neat Cement.	
24 hours in moist air	175 lbs.
7 days (1 day in moist air, 6 days in water)	500 lbs.
28 days (1 day in moist air, 27 days in water)	600 lbs.
One Part Cement, Three Parts Standard Ottawa Sand.	
7 days (1 day in moist air, 6 days in water)	200 lbs.
28 days (1 day in moist air, 27 days in water)	275 lbs.

CONSTANCY OF VOLUME.

Pats of neat cement about three inches in diameter, one-half inch thick at the center, and tapering to a thin edge, shall be kept in moist air for a period of twenty-four hours.

(*a*) A pat is then kept in air at normal temperature and observed at intervals for at least 28 days.

(*b*) Another pat is kept in water maintained as near 70° F. as practicable, and observed at intervals for at least 28 days.

(*c*) A third pat is exposed in any convenient way in an atmosphere of steam, above boiling water, in a loosely closed vessel for five hours.

These pats, to satisfactorily pass the requirements, shall remain firm and hard and show no signs of distortion, checking, cracking, or disintegrating.

SULPHURIC ACID AND MAGNESIA.

The cement shall not contain more than 1.75% of anhydrous sulphuric acid (SO_3), nor more than 4% of magnesia (MgO).

Report of Committee on Uniform Tests of Cement of the American Society of Civil Engineers.

PRESENTED AT THE ANNUAL MEETING, JANUARY 18TH, 1911.

Your Committee on Uniform Tests of Cement presents the following report:

SAMPLING

1.—*Selection of Sample.*—The selection of the sample for testing is a detail that must be left to the discretion of the engineer; the number and the quantity to be taken from each package will depend largely on the importance of the work, the number of tests to be made and the facilities for making them.

2.—The sample shall be a fair average of the contents of the package; it is recommended that, where conditions permit, one barrel in every ten be sampled.

3.—Samples should be passed through a sieve having twenty meshes per linear inch, in order to break up lumps and remove foreign material; this is also a very effective method for mixing them together in order to obtain an average. For determining the characteristics of a shipment of cement, the individual samples may be mixed and the average tested; where time will permit, however, it is recommended that they be tested separately.

4.—*Method of Sampling.*—Cement in barrels should be sampled through a hole made in the center of one of the staves, midway between the heads, or in the head, by means of an auger or a sampling iron similar to that used by sugar inspectors. If in bags, it should be taken from surface to center.

CHEMICAL ANALYSIS.

5.—*Significance.*—Chemical analysis may render valuable service in the detection of adulteration of cement with considerable amounts of inert material, such as slag or ground limestone. It is of use, also, in determining whether certain constituents, believed to be harmful when in excess of a certain percentage, as magnesia and sulphuric anhydride, are present in inadmissible proportions.

6.—The determination of the principal constituents of cement —silica, alumina, iron oxide and lime—is not conclusive as an indication of quality. Faulty character of cement results more frequently from imperfect preparation of the raw material or defective burning than from incorrect proportions of the constituents. Cement made from very finely-ground material, and thoroughly burned, may contain much more lime than the amount usually present, and still be perfectly sound. On the other hand, cements low in lime may, on account of careless preparation of the raw material, be of dangerous character. Further, the ash of the fuel used in burning may so greatly modify the composition of the product as largely to destroy the significance of the results of analysis.

7.—*Method.*—As a method to be followed for the analysis of cement, that proposed by the Committee on Uniformity in the Analysis of Materials for the Portland Cement Industry, of the New York Section of the Society for Chemical Industry, and published in *Engineering News,* Vol. 50, p. 60, 1903; and in *The Engineering Record,* Vol. 48, p. 49, 1903, is recommended.

SPECIFIC GRAVITY.

8.—*Significance.*—The specific gravity of cement is lowered by adulteration and hydration, but the adulteration must be in considerable quantity to affect the results appreciably.

9.—Inasmuch as the differences in specific gravity are usually very small, great care must be exercised in making the determination.

10.—*Apparatus and Method.*—The determination of specific gravity is most conveniently made with Le Chatelier's apparatus. This consists of a flask (*D*), Fig. 1, of 120 cu. cm. (7.32 cu. in.) capacity, the neck of which is about 20 cm. (7.87 in.) long; in the middle of this neck is a bulb (*C*), above and below which are two marks (*F*) and (*E*); the volume between these marks is 20 cu. cm. (1.22 cu. in.). The neck has a diameter of about 9 mm. (0.35 in.), and is graduated into tenths of cubic centimeters above the mark (*F*).

11.—Benzine (62° Baumé naphtha), or kerosene free from water, should be used in making the determination.

12.—The specific gravity is determined as follows:

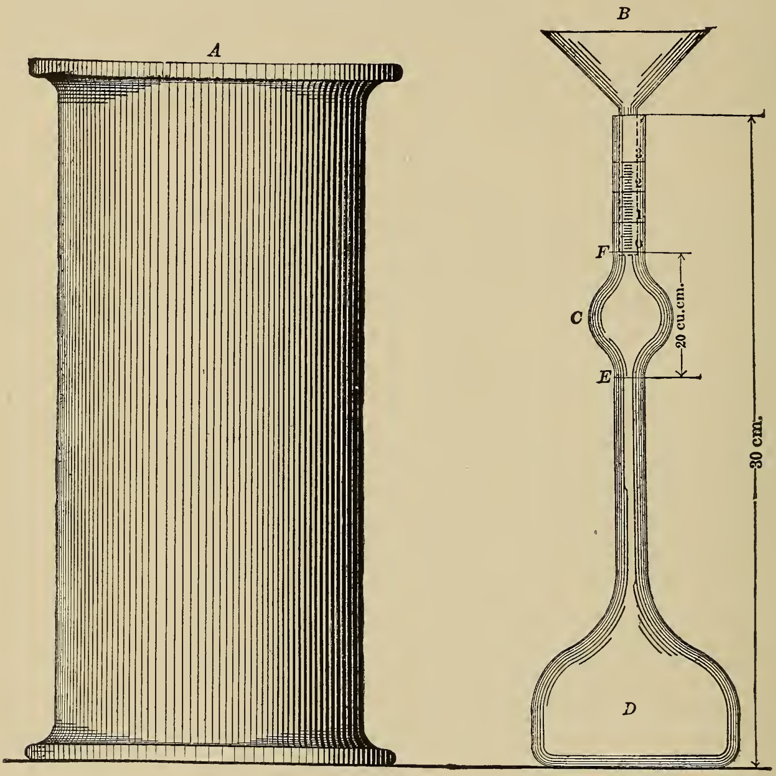
The flask is filled with either of these liquids to the lower mark (*E*), and 64 g. (2.25 oz.) of powder, cooled to the temperature of the liquid, is gradually introduced through the funnel (*B*) [the stem of which extends into the flask at the top of the bulb (*C*)], until all the powder is introduced, and the level of the liquid rises to some division of the graduated neck. This reading plus 20 cu. cm. is the volume displaced by 64 g. of the powder.

13.—The specific gravity is then obtained from the formula:

$$\text{Specific Gravity} = \frac{\text{Weight of Cement, in grammes.}}{\text{Displaced Volume, in cubic centimeters.}}$$

14.—The flask, during the operation, is kept immersed in water in a jar (*A*), in order to avoid variations in the temperature of the liquid. The results should agree within 0.01. The determination of specific gravity should be made on the cement as received; and, should it fall below 3.10, a second determination should be made on the sample ignited at a low red heat.

15.—A convenient method for cleaning the apparatus is as follows: The flask is inverted over a large vessel, preferably a glass jar, and shaken vertically until the liquid starts to flow freely; it is then held still in a vertical position until empty; the remaining traces of cement can be removed in a similar manner by pouring into the flask a small quantity of clean liquid benzine or kerosene and repeating the operation.



LE CHATELIER S SPECIFIC GRAVITY APPARATUS.

FIG. 1.

FINENESS.

16.—*Significance.*—It is generally accepted that the coarser particles in cement are practically inert, and it is only the extremely fine powder that possesses adhesive or cementing qualities. The more finely cement is pulverized, all other conditions being the same, the more sand it will carry and produce a mortar of a given strength.

17.—The degree of final pulverization which the cement receives at the place of manufacture is ascertained by measuring the residue retained on certain sieves. Those known as the No. 100 and No. 200 sieves are recommended for this purpose.

18.—*Apparatus.*—The sieves should be circular, about 20 cm. (7.87 in.) in diameter, 6 cm. (2.36 in.) high, and provided with a pan, 5 cm. (1.97 in.) deep, and a cover.

19.—The wire cloth should be of brass wire having the following diameters:

No. 100, 0.0045 in.; No. 200, 0.0024 in.

20.—This cloth should be mounted on the frames without distortion; the mesh should be regular in spacing and be within the following limits:

No. 100, 96 to 100 meshes to the linear inch.
No. 200, 188 to 200 meshes to the linear inch.

21.—Fifty grammes (1.76 oz.) or 100 g. (3.52 oz.) should be used for the test, and dried at a temperature of 100° cent. (212° Fahr.) prior to sieving.

22.—*Method.*—The thoroughly dried and coarsely screened sample is weighed and placed on the No. 200 sieve, which, with pan and cover attached, is held in one hand in a slightly inclined position, and moved forward and backward, at the same time striking the side gently with the palm of the other hand, at the rate of about 200 strokes per minute. The operation is continued until not more than one-tenth of 1% passes through after one minute of continuous sieving. The residue is weighed, then placed on the No. 100 sieve and the operation repeated. The work may be expedited by placing in the sieve a small quantity of large steel shot. The results should be reported to the nearest tenth of 1 per cent.

NORMAL CONSISTENCY.

23.—*Significance.*—The use of a proper percentage of water in making the pastes* from which pats, tests of setting, and briquettes are made, is exceedingly important, and affects vitally the results obtained.

24.—The determination consists in measuring the amount of water required to reduce the cement to a given state of plasticity, or to what is usually designated the normal consistency.

25.—The Committee recommends the following method for determining normal consistency.

26.—*Method. Vicat Needle Apparatus.*—This consists of a frame (*K*), Fig. 2, bearing a movable rod (*L*), with the cap (*A*) at one end, and at the other the cylinder (*B*), 1 cm. (0.39 in.) in diameter, the cap, rod, and cylinder weighing 300 g. (10.58 oz.). The rod, which can be held in any desired position by a screw (*F*), carries an indicator, which moves over a scale (graduated to centimeters) attached to the frame (*K*). The paste is held by a conical, hard-

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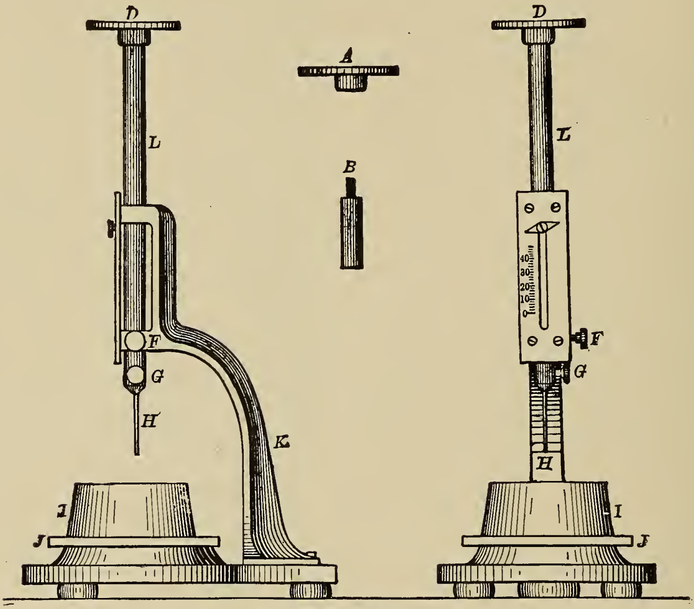
*The term "paste" is used in this report to designate a mixture of cement and water, and the word "mortar" a mixture of cement, sand and water.

rubber ring (*I*), 7 cm. (2.76 in.) in diameter at the base, 4 cm. (1.57 in.) high, resting on a glass plate (*J*), about 10 cm. (3.94 in.) square.

27.—In making the determination, the same quantity of cement as will be subsequently used for each batch in making the briquettes, but not less than 500 g., is kneaded into a paste, as described in Paragraph 52, and quickly formed into a ball with the hands, completing the operation by tossing it six times from one hand to the other, maintained 6 in. apart; the ball is then pressed into the rubber ring, through the larger opening, smoothed off, and placed (on its large end) on a glass plate and the smaller end smoothed off with a trowel; the paste, confined in the ring, resting on the plate, is placed under the rod bearing the cylinder, which is brought in contact with the surface and quickly released.



VICAT NEEDLE.
FIG. 2.

28.—The paste is of normal consistency when the cylinder in one minute from the time it is released penetrates to a point in the mass 10 mm. (0.39 in.) below the top of the ring. Great care must be taken to fill the ring exactly to the top. The apparatus must be free from all vibrations during the test.

29.—The trial pastes are made with varying percentages of water until the correct consistency is obtained.

30.—The Committee has recommended, as normal, a paste, the consistency of which is rather wet, because it believes that variations in the amount of compression to which the briquette is subjected in moulding are likely to be less with such a paste.

31.—Having determined in this manner the proper percentage of water required to produce a paste of normal consistency, the proper percentage required for the mortars is obtained from the table below.

PERCENTAGE OF WATER FOR STANDARD MORTARS.

Neat.	One cement, three standard Ottawa sand.	Neat.	One cement, three standard Ottawa sand.	Neat.	One cement, three standard Ottawa sand.
15	8.0	23	9.3	31	10.7
16	8.2	24	9.5	32	10.8
17	8.3	25	9.7	33	11.0
18	8.5	26	9.8	34	11.2
19	8.7	27	10.0	35	11.5
20	8.8	28	10.2	36	11.5
21	9.0	29	10.3	37	11.7
22	9.2	30	10.5	38	11.8

TIME OF SETTING.

32.—*Significance.*—The object of this test is to determine the time which elapses from the moment water is added until the paste ceases to be fluid and plastic (called the "initial set"), and also the time required for it to acquire a certain degree of hardness (called the "final" or "hard set"). The former of these is the more important, since, with the commencement of setting, the process of crystallization or hardening is said to begin. As a disturbance of this process may produce a loss of strength, it is desirable to complete the operation of mixing and moulding or incorporating the mortar into the work before the cement begins to set.

33.—It is usual to measure arbitrarily the beginning and end of the setting by the penetration of weighted wires of given diameters.

34.—*Method.*—For this purpose the Vicat Needle, which has already been described in Paragraph 26, should be used.

35.—In making the test, a paste of normal consistency is moulded and placed under the rod (*L*), Fig. 2, as described in Paragraph 27; this rod, bearing the cap (*D*) at one end and the needle (*H*), 1 mm. (0.039 in.) in diameter, at the other, weighing 300 g. (10.58 oz.). The needle is then carefully brought in contact with the surface of the paste and quickly released.

36.—The setting is said to have commenced when the needle ceases to pass a point 5 mm. (0.20 in.) above the upper surface of the glass plate, and is said to have terminated the moment the needle does not sink visibly into the mass.

37.—The test pieces should be stored in moist air during the test; this is accomplished by placing them on a rack over water contained in a pan and covered with a damp cloth, the cloth to be kept away from them by means of a wire screen; or they may be stored in a moist box or closet.

38.—Care should be taken to keep the needle clean, as the collection of cement on the sides of the needle retards the penetration, while cement on the point reduces the area and tends to increase the penetration.

39.—The determination of the time of setting is only approximate, being materially affected by the temperature of the mixing water, the temperature and humidity of the air during the test, the percentage of water used, and the amount of kneading the paste receives.

STANDARD SAND.

40.—The Committee recommends the natural sand from Ottawa, Ill., screened to pass a sieve having 20 meshes per linear inch and retained on a sieve having 30 meshes per linear inch; the wires to have diameters of 0.0165 and 0.0112 in., respectively, *i. e.,* half the width of the opening in each case. Sand having passed the No. 20 sieve shall be considered standard when not more than 1% passes a No. 30 sieve after one minute's continuous sifting of a 500-g. sample*.

FORM OF TEST PIECES.

41.—For tension tests the Committee recommends the form of test piece shown in Fig. 3.

42.—For compression tests a 2-in. cube is recommended.

MOULDS.

43.—The moulds should be made of brass, bronze, or some equally non-corrodible material, having sufficient metal in the sides to prevent spreading during moulding.

44.—Gang moulds, which permit moulding a number of briquettes at one time, are preferred by many to single moulds; since the greater quantity of mortar that can be mixed tends to produce greater uniformity in the results. The type shown in Fig. 4 is recommended.

45.—The moulds should be wiped with an oily cloth before using.

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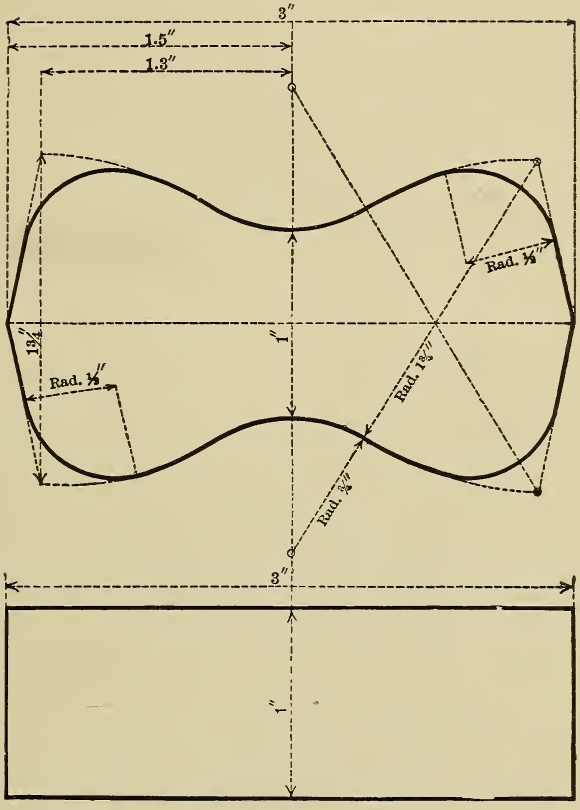
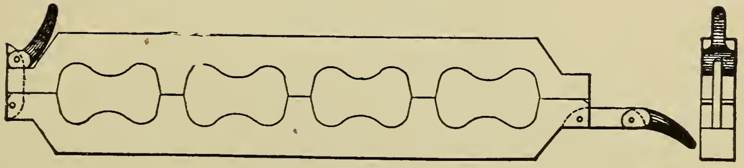
*This sand may be obtained from the Ottawa Silica Company at a cost of two cents per pound, f. o. b. cars, Ottawa, Illinois.



DETAILS FOR BRIQUETTE.

FIG. 3.



DETAILS FOR GANG MOULD.

FIG. 4.

MIXING.

46.—All proportions should be stated by weight; the quantity of water to be used should be stated as a percentage of the dry material.

47.—The metric system is recommended because of the convenient relation of the gramme and the cubic centimeter.

48.—The temperature of the room and the mixing water should be as near 21° cent. (70° Fahr.) as it is practicable to maintain it.

49.—The sand and cement should be thoroughly mixed dry. The mixing should be done on some non-absorbing surface, preferably plate glass. If the mixing must be done on an absorbing surface it should be thoroughly dampened prior to use.

50.—The quantity of material to be mixed at one time depends on the number of test pieces to be made; about 1,000 g. (35.28 oz.) makes a convenient quantity to mix, especially by hand methods.

51.—The Committee, after investigation of the various mechanical mixing machines, has decided not to recommend any machine that has thus far been devised, for the following reasons:

(1) The tendency of most cement is to "ball up" in the machine, thereby preventing the working of it into a homogeneous paste; (2) there is no means of ascertaining when the mixing is complete without stopping the machine, and (3) the difficulty of keeping the machine clean.

52.—*Method.*—The material is weighed and placed on the mixing table, and a crater formed in the center, into which the proper percentage of clean water is poured; the material on the outer edge is turned into the crater by the aid of a trowel. As soon as the water has been absorbed, which should not require more than one minute, the operation is completed by vigorously kneading with the hands for an additional one minute, the process being similar to that used in kneading dough. A sand-glass affords a convenient guide for the time of kneading. During the operation of mixing, the hands should be protected by gloves, preferably of rubber.

MOULDING.

53.—Having worked the paste or mortar to the proper consistency, it is at once placed in the moulds by hand.

54.—The Committee has been unable to secure satisfactory results with the present moulding machines; the operation of machine moulding is very slow, and the present types permit of moulding but one briquette at a time, and are not practicable with the pastes or mortars herein recommended.

55.—*Method.*—The moulds should be filled immediately after the mixing is completed, the material pressed in firmly with the fingers and smoothed off with a trowel without mechanical ramming; the material should be heaped up on the upper surface of the mould, and, in smoothing off, the trowel should be drawn over the mould in such a manner as to exert a moderate pressure on the excess material. The mould should be turned over and the operation repeated.

56.—A check upon the uniformity of the mixing and moulding is afforded by weighing the briquettes just prior to immersion, or upon removal from the moist closet. Briquettes which vary in weight more than 3% from the average should not be tested.

STORAGE OF THE TEST PIECES.

57.—During the first 24 hours after moulding, the test pieces should be kept in moist air to prevent them from drying out.

58.—A moist closet or chamber is so easily devised that the use of the damp cloth should be abandoned. Covering the test pieces with a damp cloth is objectionable, as commonly used, because the cloth may dry out unequally, and, in consequence, the test pieces are not all maintained under the same condition. Where a moist closet is not available, a cloth may be used and kept uniformly wet by immersing the ends in water. It should be kept from direct contact with the test pieces by means of a wire screen or some similar arrangement.

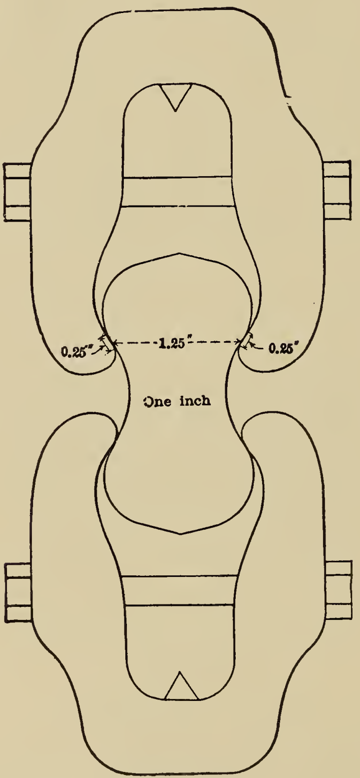
59.—A moist closet consists of a soapstone or slate box, or a metal-lined wooden box—the metal lining being covered with felt and this felt kept wet. The bottom of the box is so constructed as to hold water, and the sides are provided with cleats for holding glass shelves on which to place the briquettes. Care should be taken to keep the air in the closet uniformly moist.

60.—After 24 hours in moist air, the test pieces for longer periods of time should be immersed in water maintained as near 21° cent. (70° Fahr.) as practicable; they may be stored in tanks or pans, which should be of non-corrodible material.

TENSILE STRENGTH.

61.—The tests may be made on any machine. A solid metal clip, as shown in Fig. 5, is recommended. This clip is to be used without cushioning at the points of contact with the test specimen. The bearing at each point of contact should be ¼ in. wide, and the distance between the center of contact on the same clip should be 1¼ in.

62.—Test pieces should be broken as soon as they are removed from the water. Care should be observed in centering the briquettes in the testing machine, as cross-strains, produced by improper centering, tend to lower the breaking strength. The load should not be applied too suddenly, as it may produce vibration, the shock from which often breaks the briquettes before the ultimate strength is reached. Care must be taken that the clips and the sides of the briquette be clean and free from grains of sand or dirt, which would prevent a good bearing. The load should be applied at the rate of 600 lb. per min. The average of the briquettes of each sample tested should be taken as the test, excluding any results which are manifestly faulty.



FORM OF CLIP.

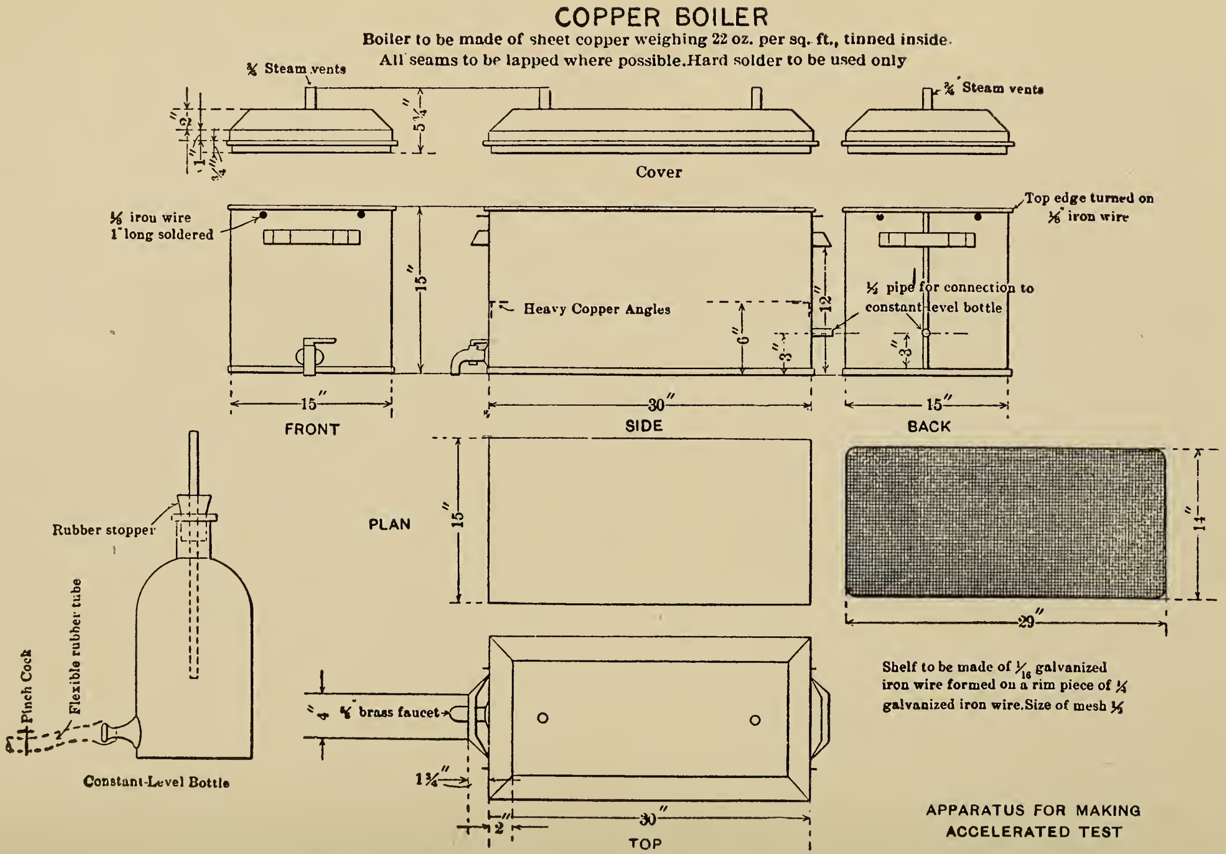
Fig. 5.

CONSTANCY OF VOLUME.

63.—*Significance.*—The object is to develop those qualities which tend to destroy the strength and durability of a cement. As it is highly essential to determine such qualities at once, tests of this character are for the most part made in a very short time, and are known, therefore, as accelerated tests. Failure is revealed by cracking, checking, swelling, or disintegration, or all of these phenomena. A cement which remains perfectly sound is said to be of constant volume.

64.—*Methods.*—Tests for constancy of volume are divided into two classes: (1) normal tests, or those made in either air or water maintained at about 21° cent. (70° Fahr.), and (2) accelerated tests, or those made in air, steam, or water at a temperature of 45° cent. (113° Fahr.) and upward. The test pieces should be allowed to remain 24 hours in moist air before immersion in water or steam, or preservation in air.

65.—For these tests, pats, about 7½ cm. (2.95 in. in diameter, 1¼ cm. (0.49 in.) thick at the center, and tapering to a thin edge,



To be made of sheet copper weighing 22 oz. per sq. ft., tinned inside.
All seams to be lapped where possible. Hard solder only to be used.

FIG. 8.

should be made, upon a clean glass plate [about 10 cm. (3.94 in.) square], from cement paste of normal consistency.

66.—*Normal Test.*—A pat is immersed in water maintained as near 21° cent. (70° Fahr.) as possible for 28 days, and observed at intervals. A similar pat, after 24 hours in moist air, is maintained in air at ordinary temperature and observed at intervals.

67.—*Accelerated Test.*—A pat is placed in an atmosphere of steam upon a wire screen 1 in. above boiling water for five (5) hours. The apparatus should be so constructed as to permit the free escape of steam and maintain atmospheric pressure. Since the type of apparatus used has a great influence on the uniformity of the results, that shown in Fig. 8 is recommended.

68.—To pass these tests satisfactorily, the pats should remain firm and hard, and show no signs of cracking, distortion or disintegration.

69.—Should the pat leave the plate, distortion may be detected best with a straight-edge applied to the surface which was in contact with the plate.

70.—In the present state of our knowledge it cannot be said that cement should necessarily be condemned simply for failure to pass the accelerated tests; nor can a cement be considered entirely satisfactory simply because it has passed these tests.

Submitted on behalf of the Committee,

GEORGE S. WEBSTER,
Chairman.
RICHARD L. HUMPHREY,
Secretary.

JANUARY 18TH, 1911.

Committee.
GEORGE S. WEBSTER,
RICHARD L. HUMPHREY,
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F. H. LEWIS.

Reprint of Report Authorized by the Society.

New York Section Society for Chemical Industry

METHOD SUGGESTED FOR THE ANALYSIS OF LIMESTONES, RAW MIXTURES AND PORTLAND CEMENTS BY THE COMMITTEE ON UNIFORMITY IN TECHNICAL ANALYSIS WITH THE ADVICE OF W. F. HILLEBRAND.

SOLUTION.

One-half gram of the finely-powdered substance is to be weighed out and, if a limestone or unburned mixture, strongly ignited in a covered platinum crucible over a strong blast for fifteen minutes, or longer if the blast is not powerful enough to effect complete conversion to a cement in this time. It is then transferred to an evaporating dish, preferably a platinum for the sake of celerity in evaporation, moistened with enough water to prevent lumping, and 5 to 10 c. c. of strong HCl added and digested with the aid of gentle heat and agitation until solution is complete. Solution may be aided by light pressure with the flattened end of a glass rod.* The solution is then evaporated to dryness, as far as this may be possible on the bath.

SILICA (SiO_2).

The residue without further heating is treated at first with 5 to 10 c. c. of strong HCl, which is then diluted to half strength or less, or upon the residue may be poured at once a larger volume of acid of half strength. The dish is then covered and digestion allowed to go on for 10 minutes on the bath, after which the solution is filtered and the separated silica washed thoroughly with water. The filtrate is again evaporated to dryness, the residue without further heating, taken up with acid and water and the small amount of silica it contains separated on another filter paper. The papers containing the residue are transferred wet to a weighed platinum crucible, dried, ignited, first over a Bunsen burner until the carbon of the filter is completely consumed, and finally over the blast for 15 minutes and checked by a further blasting for 10 minutes or to constant weight.

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*If anything remains undecomposed it should be separated, fused with a little Na_2CO_3, dissolved and added to the original solution. Of course a small amount of separated non-gelatinous silica is not to be mistaken for undecomposed matter.

The silica, if great accuracy is desired, is treated in the crucible with about 10 c. c. of HFl and four drops of H_2SO_4 and evaporated over a low flame to complete dryness. The small residue is finally blasted, for a minute or two, cooled and weighed. The difference between this weight and the weight previously obtained gives the amount of silica.*

ALUMINA AND IRON (Al_2O_3 AND Fe_2O_3).

The filtrate, about 250 c. c., from the second evaporation for SiO_2, is made alkaline with NH_4OH after adding HCl, if need be, to insure a total of 10 to 15 c. c. strong acid, and boiled to expel excess of NH_3, or until there is but a faint odor of it, and the precipitate iron and aluminum hydrates, after settling, are washed once by decantation and slightly on the filter. Setting aside the filtrate, the precipitate is dissolved in hot dilute HCl, the solution passing into the beaker in which the precipitation was made. The aluminum and iron are then reprecipitated by NH_4OH, boiled and the second precipitate collected and washed on the same filter used in the first instance. The filter paper, with the precipitate, is then placed in a weighed platinum crucible, the paper burned off and the precipitate ignited and finally blasted 5 minutes, with care to prevent reduction, cooled and weighed as $Al_2O_3+Fe_2O_3$.†

IRON (Fe_2O_3).

The combined iron and aluminum oxides are fused in a platinum crucible at a very low temperature with about 3 to 4 grams of $KHSO_4$, or, better, $NaHSO_4$, the melt taken up with so much dilute H_2SO_4 that there shall be no less than 5 grams absolute acid and enough water to effect solution on heating. The solution is then evaporated and eventually heated till acid fumes come off copiously. After cooling and redissolving in water the small amount of silica is filtered out, weighed and corrected by HFl and H_2SO_4.‡ The filtrate is reduced by zinc, or preferably by hydrogen sulphide, boiling out the excess of the latter afterwards while passing CO_2 through the flask, and titrated with permanganate.§ The strength of the permanganate solution should not be greater than .0040 gr. Fe_2O_3 per c. c.

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*For ordinary control in the plant laboratory this correction may, perhaps, be neglected; the double evaporation never.

†This precipitate contains TiO_2, P_2O_5, Mn_3O_4.

‡This correction of Al_2O_3 Fe_2O_3 for silica should not be made when the HFl correction of the main silica has been omitted, unless that silica was obtained by only one evaporation and filtration. After two evaporations and filtrations 1 to 2 mg. of SiO are still to be found with the Al_2O_3 Fe_2O_3.

§In this way only is the influence of titanium to be avoided and a correct result obtained for iron.

LIME (CaO).

To the combined filtrate from the $Al_2O_3+Fe_2O_3$ precipitate a few drops of NH_4OH are added, and the solution brought to boiling. To the boiling solution 20 c. c. of a saturated solution of ammonium oxalate are added, and the boiling continued until the precipitated CaC_2O_4 assumes a well-defined granular form. It is then allowed to stand for 20 minutes, or until the precipitate has settled, and then filtered and washed. The precipitate and filter are placed wet in a platinum crucible, and the paper burned off over a small flame of a Bunsen burner. It is then ignited, redissolved in HCl, and the solution made up to 100 c c. with water. Ammonia is added in slight excess, and the liquid is boiled. If a small amount of Al_2O_3 separates, this is filtered out, weighed, and the amount added to that found in the first determination, when greater accuracy is desired. The lime is then reprecipitated by ammonium oxalate, allowed to stand until settled, filtered, and washed,* weighed as oxide by ignition and blasted in a covered crucible to constant weight, or determined with dilute standard permanganate.†

MAGNESIA (MgO).

The combined filtrates from the calcium precipitates are acidified with HCl and concentrated on the steam bath to about 150 c. c., 10 c. c. of saturated solution of $Na(NH_4)HPO_4$ are added, and the solution boiled for several minutes. It is then removed from the flame and cooled by placing the beaker in ice water. After cooling, NH_4OH is added drop by drop with constant stirring until the crystalline ammonium-magnesium ortho-phosphate begins to form, and then in moderate excess, the stirring being continued for several minutes. It is then set aside for several hours in a cool atmosphere and filtered. The precipitate is redissolved in hot dilute HCl, the solution made up to about 100 c. c., 1 c. c. of a saturated solution of $Na(NH_4)HPO_4$ added, and ammonia drop by drop, with constant stirring until the precipitate is again formed as described and the ammonia is in moderate excess. It is then allowed to stand for about 2 hours, when it is filtered on a paper or a Gooch crucible, ignited, cooled and weighed as $Mg_2P_2O_7$.

ALKALIES (K_2O and Na_2O).

For the determination of the alkalies, the well-known method of Prof. J. Lawrence Smith is to be followed, either with or without the addition of $CaCO_3$ with NH_4Cl.

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*The volume of wash-water should not be too large; vide Hillebrand.

†The accuracy of this method admits of criticism, but its convenience and rapidity demand its insertion.

ANHYDROUS SULPHURIC ACID (SO_3).

One gram of the substance is dissolved in 15 c. c. of HCl, filtered and residue washed thoroughly.*

The solution is made up to 250 c. c. in a beaker and boiled. To the boiling solution 10 c. c. of a saturated solution of $BaCl_2$ is added slowly drop by drop from a pipette and the boiling continued until the precipitate is well formed, or digestion on the steam bath may be substituted for the boiling. It is then set aside over night, or for a few hours, filtered, ignited and weighed as $BaSO_4$.

TOTAL SULPHUR.

One gram of the material is weighed out in a large platinum crucible and fused with Na_2CO_3 and a little KNO_3, being careful to avoid contamination from sulphur in the gases from source of heat. This may be done by fitting the crucible in a hole in an asbestos board. The melt is treated in the crucible with boiling water and the liquid poured into a tall narrow beaker and more hot water added until the mass is disintegrated. The solution is then filtered. The filtrate contained in a No. 4 beaker is to be acidulated with HCl and made up to 250 c. c. with distilled water, boiled, the sulphur precipitated as $BaSO_4$ and allowed to stand over night or for a few hours.

LOSS ON IGNITION.

Half a gram of cement is to be weighed out in a platinum crucible, placed in a hole in an asbestos board so that about $\frac{3}{5}$ of the crucible projects below, and blasted 15 minutes, preferably with an inclined flame. The loss by weight, which is checked by a second blasting of 5 minutes, is the loss on ignition.

May, 1903: Recent investigations have shown that large errors in results are often due to the use of impure distilled water and reagents. The analyst should, therefore, test his distilled water by evaporation and his reagents by appropriate tests before proceeding with his work.

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*Evaporation to dryness is unnecessary, unless gelatinous silica should have separated and should never be performed on a bath heated by gas; vide Hillebrand.