

DEPARTMENT OF COMMERCE

CIRCULAR
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 33

**UNITED STATES GOVERNMENT SPECIFICATION
FOR PORTLAND CEMENT**

[2d Edition]

Issued July 1, 1913



WASHINGTON
GOVERNMENT PRINTING OFFICE

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EXECUTIVE ORDER

It is hereby ordered that all Portland cement that may hereafter be purchased by any Department, Bureau, Office, or independent establishment of the Government, or that may be used in construction work connected with any of the aforesaid branches of the Government service, shall conform in every respect to the specification for Portland cement adopted by the Departmental Conference at the meeting held at the Bureau of Standards on February 13, 1912, and approved by the heads of the several departments (to be known as the United States Government Specification for Portland Cement): Provided, however, that such specification may be modified from time to time by any similar Departmental conference, with the approval of the heads of the several Departments.

WM H TAFT

THE WHITE HOUSE,
April 30, 1912.

INTRODUCTORY STATEMENT

In June, 1911, the Secretary of the Department of Commerce and Labor arranged, through the Secretaries of the various departments, for a conference of Government engineers for the purpose of unifying the specifications for Portland cement used by the United States Government. At this conference a committee was appointed to consider existing specifications and to recommend a single specification for Portland cement to be used by all departments of the Government.

After an extended series of meetings of this committee, at which careful consideration was given to representative specifications for Portland cement, as well as to all available data on methods of tests, a tentative specification was developed, which was reported to the departmental conference at a general meeting held July 20, 1911.

In view of the desirability of agreement between the specifications in use by the public and those adopted by the Government, the committee was instructed by the conference to confer with representative consumers and manufacturers as well as the special committees of the national engineering societies more directly interested in the subject of cement specifications. As a result the tentative specifications first reported by the departmental committee were modified slightly, until substantial agreement was reached on practically all points except the methods of determining the normal consistency and time of setting, and the following specifications were unanimously adopted by the departmental conference at the meeting held February 13, 1912.

It was recognized that no specification can be considered final, but must be subject to revision from time to time as occasion requires, and provision will be made for such revision by the various Government departments, all of which have adopted the specification as recommended by the conference.

S. W. STRATTON,
Director.

Approved:
A. L. THURMAN,
Acting Secretary.

DEPARTMENTAL CONFERENCE AND COMMITTEE*

NAME	REPRESENTING
S. W. Stratton , <i>Chairman of Conference</i>	Bureau of Standards, Department of Commerce and Labor
Rudolph J. Wig , <i>Secretary of Conference</i>	Bureau of Standards, Department of Commerce and Labor
Spencer Cosby , Colonel, U. S. Army	Office of Chief of Engineers, War Department
In charge of Public Buildings and Grounds, District of Columbia	
W. A. E. Doying	Isthmian Canal Commission, War Department
Inspecting Engineer, Isthmian Canal Commission	
B. F. Cheatham , Major, U. S. Army	Quartermaster Corps, War Department
Quartermaster Corps	
F. B. Wheaton	Office of the Quartermaster General, War Department
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Assistant Engineer, Sewer Department, District of Columbia	
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Supt. of Computing Division, Office of Supervising Architect	
H. C. Heald	Office of Supervising Architect, Treasury Department
Structural Engineer, Office of Supervising Architect	
W. H. Rose , Captain, U. S. Army	Alternate in absence of Col. Spencer Cosby
Director of Mechanical Engineering, Engineers School, Washington Barracks	
S. S. Hunt , Captain, U. S. Army	Office of Superintendent of United States Capitol Building and Grounds
Constructor, Office of Superintendent of United States Capitol Building and Grounds	
P. H. Bates	Bureau of Standards, Department of Commerce and Labor
Chemist, Bureau of Standards	
S. Voorhees	Alternate in absence of P. H. Bates
Engineer Chemist, Bureau of Standards	

COMMITTEE APPOINTED TO DRAFT THE SPECIFICATIONS

A. P. Davis , <i>Chairman</i>	Carl A. Carlson
Rudolph J. Wig , <i>Secretary</i>	Asa E. Phillips
Spencer Cosby	S. S. Voorhees
W. H. Rose ,	W. A. E. Doying
James C. Plant	

* As constituted July 1, 1911.

UNITED STATES GOVERNMENT SPECIFICATION FOR PORTLAND CEMENT

I. SPECIFICATION

DEFINITION

1. The cement shall be the product obtained by finely pulverizing clinker produced by calcining to incipient fusion, an intimate mixture of properly proportioned argillaceous and calcareous substances, with only such additions subsequent to calcining as may be necessary to control certain properties. Such additions shall not exceed 3 per cent, by weight, of the calcined product.

COMPOSITION

2. In the finished cement, the following limits shall not be exceeded:

	Per cent
Loss on ignition for 15 minutes.....	4
Insoluble residue.....	1
Sulphuric anhydride (SO ₃).....	1.75
Magnesia (MgO).....	4

SPECIFIC GRAVITY

3. The specific gravity of the cement shall be not less than 3.10. Should the cement as received fall below this requirement, a second test may be made upon a sample heated for 30 minutes at a very dull red heat.

FINENESS

4. Ninety-two per cent of the cement, by weight, shall pass through the No. 100 sieve, and 75 per cent shall pass through the No. 200 sieve.

SOUNDNESS

5. Pats of neat cement prepared and treated as hereinafter prescribed shall remain firm and hard and show no sign of distortion, checking, cracking, or disintegrating. If the cement fails to meet the prescribed steaming test, the cement may be rejected or the steaming test repeated after seven or more days at the option of the engineer.

TIME OF SETTING

6. The cement shall not acquire its initial set in less than 45 minutes and must have acquired its final set within 10 hours.

TENSILE STRENGTH

7. Briquettes made of neat cement, after being kept in moist air for 24 hours and the rest of the time in water, shall develop tensile strength per square inch as follows:

	Pounds
After 7 days.....	500
After 28 days.....	600

8. Briquettes made up of 1 part cement and 3 parts standard Ottawa sand, by weight, shall develop tensile strength per square inch as follows:

	Pounds
After 7 days.....	200
After 28 days.....	275

9. The average of the tensile strengths developed at each age by the briquettes in any set made from one sample is to be considered the strength of the sample at that age, excluding any results that are manifestly faulty.

10. The average strength of the sand mortar briquettes at 28 days shall show an increase over the average strength at 7 days.

BRAND

11. Bids for furnishing cement or for doing work in which cement is to be used shall state the brand of cement proposed to be furnished and the mill at which made. The right is reserved to reject any cement which has not established itself as a high-grade Portland cement, and has not been made by the same mill for two years and given satisfaction in use for at least one year under climatic and other conditions at least equal in severity to those of the work proposed.

PACKAGES

12. The cement shall be delivered in sacks, barrels, or other suitable packages (to be specified by the engineer), and shall be dry and free from lumps. Each package shall be plainly labeled with the name of the brand and of the manufacturer.

13. A sack of cement shall contain 94 pounds net. A barrel shall contain 376 pounds net. Any package that is short weight or broken or that contains damaged cement may be rejected, or accepted as a fractional package, at the option of the engineer.

INSPECTION

14. The cement shall be tested in accordance with the standard methods hereinafter prescribed. In general the cement will be inspected and tested after delivery, but partial or complete inspection at the mill may be called for in the specifications or contract. Tests may be made to determine the chemical composition, specific gravity, fineness, soundness, time of setting, and tensile strength, and a cement may be rejected in case it fails to meet any of the specified requirements. An agent of the contractor may be present at the making of the tests or they may be repeated in his presence.

15. In case of the failure of any of the tests, and if the contractor so desires, the engineer may, if he deem it to the interest of the United States, have any or all of the tests made or repeated by the Bureau of Standards, United States Department of Commerce, in the manner hereinafter specified, all expenses of such tests to be paid by the contractor. All such tests shall be made on samples furnished by the engineer.

STANDARD METHODS OF TESTING

SAMPLING

16. The selection of the samples for testing will be left to the engineer. The number of packages sampled and the quantity to be taken from each package will depend on the importance of the work, the number of tests to be made, and the facilities for making them.

17. The samples should be so taken as to represent fairly the material, and, where conditions permit, at least 1 barrel in every 50 should be sampled. Before tests are made samples shall be passed through a sieve having 20 meshes per linear inch to remove foreign material. Samples shall be tested separately for physical qualities, but for chemical analysis mixed samples may be used. Every sample should be tested for soundness, but the number of tests for other qualities will be left to the discretion of the engineer.

CHEMICAL ANALYSIS

18. The method to be followed for the analysis of cement shall be that proposed by the Committee on Uniformity in the Analysis of Materials for the Portland Cement Industry, reported in the Journal of the Society for Chemical Industry, volume 21, page 12, 1902, and published in Engineering News, volume 50, page 60, 1903, and in the Engineering Record, volume 48, page 49, 1903.

19. The insoluble residue shall be determined on a 1-gram sample, which is digested on the steam bath in hydrochloric acid of approximately 1.035 specific gravity until the cement is dissolved. The residue is filtered, washed with hot water, and the filter-paper contents digested on the steam bath in a 5 per cent solution of sodium carbonate. The residue is then filtered, washed with hot water, then with hot hydrochloric acid, approximately of 1.035 specific gravity, and finally with hot water, then ignited and weighed. The quantity so obtained is the insoluble residue.

DETERMINATION OF SPECIFIC GRAVITY

20. The determination of specific gravity may be made with a standardized apparatus of Le Chatelier or other equally accurate form. Benzine (62° Baumé naphtha), or kerosene free from water, should be used in making the determination. The cement should be allowed to pass slowly into the liquid of the volumometer, taking care that the powder does not adhere to the sides of the graduated tube above the liquid and that the funnel through which it is introduced does not touch the liquid. The temperature

of the liquid in the flask should not vary more than 1°F during the operation. To this end the flask should be immersed in water. The results of repeated tests should agree within 0.01.

21. If the specific gravity of the cement as received is less than 3.10, a redetermination may be made as follows:

Seventy grams of the cement is placed in a nickel or platinum crucible about 2 inches in diameter and heated for 30 minutes at a temperature between 419°C and 630°C . After the cement has cooled to atmospheric temperature the specific gravity shall be determined in the same manner as described above. The cement should be heated in a muffle or other suitable furnace, the temperature of which is to be maintained above the melting point of zinc (419°C) but below the melting point of antimony (630°C). This maximum temperature can be recognized as a very dull red which is just discernible in the dark.

DETERMINATION OF FINENESS

22. The No. 100 and No. 200 sieves shall conform to the standard sieve specifications of the Bureau of Standards, Department of Commerce.

23. The determination of fineness should be made on a 50-gram sample, which may be dried at a temperature of 100°C (212°F) prior to sifting. The coarsely screened sample should be weighed and placed on the No. 200 sieve, which, with the pan and cover attached should be held in one hand in a slightly inclined position and moved forward and backward in the plane of inclination, at the same time striking the side gently about 200 times per minute against the palm of the other hand on the upstroke. The operation is to be continued until not more than 0.05 gram will pass through in one minute. The residue should be weighed, then placed on the No. 100 sieve, and the operation repeated. The sieves should be thoroughly dry and clean. Determination of fineness may be made by washing the cement through the sieve or by a mechanical sifting device which has been previously standardized with the results obtained by hand sifting on equivalent samples. In case of the failure of the cement to pass the fineness requirements by the washing method or the mechanical device, it shall be tested by hand.

MIXING CEMENT PASTES AND MORTARS

24. The quantity of cement or cement and sand to be used in the paste or mortar should be expressed in grams and the quantity of water in cubic centimeters. The material should be weighed, placed upon a nonabsorbent surface, thoroughly mixed dry if sand be used, and a crater formed in the center, into which the proper percentage of clean water should be poured; the material on the outer edge should be turned into the crater by the aid of a trowel. As soon as the water has been absorbed, the operation should be completed by vigorously mixing with the hands for one minute and a

half. During the operation of mixing, the hands should be protected by rubber gloves. The temperature of the room and the mixing water should be maintained as nearly as practicable at 21° C (70° F).

DETERMINATION OF NORMAL CONSISTENCY

25. The normal consistency for neat paste to be used in making briquettes and pats should be determined by the ball method, as follows:

26. A quantity of cement paste should be mixed in the manner above described under Mixing Cement Pastes and Mortars, and quickly formed into a ball about 2 inches in diameter. The ball should then be dropped upon a hard, smooth, and flat surface from a height of 2 feet. The paste is of normal consistency when the ball does not crack and does not flatten more than one-half of its original diameter.

27. Trial pastes should be made with varying percentages of water until the correct consistency is obtained.

28. The percentage of water to be used in mixing mortars for sand briquettes is given by the formula:

$$y = \frac{2}{3} \frac{P}{n + 1} + K$$

in which y is the percentage of water required for the sand mortar, P is the percentage of water required for neat cement paste of normal consistency,

n is the number of parts of sand to one of cement by weight, and K is a constant which for standard Ottawa sand has the value 6.5.

The percentage of water to be used for mortars containing 3 parts standard Ottawa sand, by weight, to 1 of cement is indicated in the following statement:

Percentage of water for neat cement paste	Percentage of water for 1 to 3 mortars of standard Ottawa sand
18.....	9.5
19.....	9.7
20.....	9.8
21.....	10.0
22.....	10.2
23.....	10.3
24.....	10.5
25.....	10.7
26.....	10.8
27.....	11.0
28.....	11.2
29.....	11.3

DETERMINATION OF SOUNDNESS

29. Pats of neat cement paste of normal consistency about 3 inches in diameter, one-half inch in thickness at the center, and tapering to a thin edge, should be kept in moist air for a period of 24 hours. One pat should then be kept in air and a second in water, at the ordinary temperature of

the laboratory not to vary greatly from 21°C (70°F), and both observed at intervals for at least 28 days. A third pat should be exposed to steam at atmospheric pressure above boiling water for 5 hours.

DETERMINATION OF TIME OF SETTING

30. The time of setting should be determined by the standardized Gillmore needles, as follows: A pat of neat cement paste about 3 inches in diameter and one-half inch in thickness with flat top, mixed at normal consistency should be kept in moist air, at a temperature maintained as nearly as practicable at 21°C (70°F). The cement is considered to have acquired its initial set when the pat will bear, without appreciable indentation, a needle one-twelfth of an inch in diameter loaded to weigh one-fourth of a pound. The final set has been acquired when the pat will bear without appreciable indentation, a needle one twenty-fourth of an inch in diameter, loaded to weigh 1 pound. In making the test the needle should be held in a vertical position and applied lightly to the surface of the pat. The pats made for the soundness test may be used to determine the time of setting.

TENSILE TESTS

31. Tensile tests should be made on an approved machine. The test pieces shall be briquettes of the form recommended by the Committee on Uniform Tests of Cement of the American Society of Civil Engineers, and illustrated in Circular 33 of the Bureau of Standards. The briquettes shall be made of paste or mortar of normal consistency. Immediately after mixing, the paste or mortar should be placed in the molds, pressed in firmly by the fingers and smoothed off with a trowel without mechanical ramming. The material should be heaped above the mold, and in smoothing off, the trowel should be drawn over the mold in such a manner as to exert a moderate pressure on the material. The molds should be turned over and the operation of heaping and smoothing off repeated. Not less than three briquettes should be made and tested for each sample for each period of test. The neat tests are not considered so important as the sand tests. The briquettes should be broken as soon as they are removed from the water. The load should be applied at the rate of 600 pounds per minute.

STORAGE OF TEST PIECES

32. During the first 24 hours after molding the test pieces should be kept in air sufficiently moist to prevent them from drying. After 24 hours in moist air the test pieces should be immersed in water. The air and water should be maintained as nearly as practicable at 21°C (70°F).

STANDARD SAND

33. The sand to be used shall be natural sand from Ottawa, Ill., screened to pass a No. 20 sieve and retained on a No. 30 sieve.

34. Sand having passed the No. 20 sieve shall be considered standard when not more than 2 grams pass the No. 30 sieve after one minute continuous sifting of a 200-gram sample.

35. The No. 20 and No. 30 sieves shall conform to the standard sieve specifications of the Bureau of Standards, Department of Commerce.

II. METHODS OF CHEMICAL ANALYSIS

PREFATORY NOTE

While it may not be necessary to follow the standard method of analysis in routine tests when only a general indication of composition is desired, this method, including all precautions as stated in footnotes and italicized text, must always be followed when the results are to be used as the basis for rejection, or when an accurate knowledge of composition is desired.

The standard method can only yield accurate results in the hands of a careful and experienced analyst when all precautions are properly observed and even under these conditions the results obtained in the determinations of magnesia (MgO), sulphuric anhydride (SO_3), "loss on ignition" and "insoluble residue" may be ± 0.10 per cent in error, while in general results reported for magnesia tend to be too high. Under less favorable conditions the errors may be of much greater magnitude.

It is desired to emphasize these points so as to prevent rejection of material if the specified limits are exceeded by less than 0.10 per cent.

CHEMICAL ANALYSIS

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

Report of Subcommittee (New York Section Society of Chemical Industry) on Uniformity in Analysis of Materials for the Portland Cement Industry¹

(All matter printed in italics, both in text and footnotes, has been added during the preparation of this circular at the suggestion and with the approval of W. F. Hillebrand, with special application to the analysis of Portland cement.)

SOLUTION

One-half gram² 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 15 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 of platinum for the sake of celerity in evaporation, moistened with enough water to prevent lumping, and 5 to 10 cc of strong HCl added and digested with the

¹ The original method was reported in the Journal of the Society for Chemical Industry, vol. 21, p. 30, but the method was subsequently modified by the committee and the above text practically conforms to that in the Engineering Record, vol. 48, p. 49; Engineering News, vol. 50, p. 60.

² If a limestone, 0.75 gram should be used, the approximate equivalent of 0.5 gram of cement.

aid of gentle heat and agitation until solution is completed. Solution may be aided by light pressure with the flattened end of a glass rod.³ 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 cc 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.

The silica, if great accuracy is desired, is treated in the crucible with about 10 cc of HF and 4 drops ⁴ 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.⁵

ALUMINA AND IRON (Al_2O_3 AND Fe_2O_3)

The filtrate, about 250 cc 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 cc strong acid,⁶ and boiled to expel excess of NH_3 , or until there is but a faint odor of it, and the precipitated iron and aluminum hydroxides, 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 ,⁶ boiled and the second precipitate collected and washed on the filter used in the first instance. The filter paper with the precipitate is then placed in a weighed platinum crucible (*the one containing the residue from the silica if this was corrected by hydrofluoric acid treatment*), the paper burned off, and the precipitate ignited and finally blasted 5 minutes, with care to prevent reduction, cooled and weighed as $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$.⁷

³ 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 nongelatinous silica is not to be mistaken for undecomposed matter.

⁴ 5 cc HF and 2 drops H_2SO_4 are sufficient.

⁵ For ordinary control in the plant laboratory this correction may, perhaps, be neglected; the double evaporation never. The silica so found does not represent quite all in the material under analysis; a little has passed into the filtrate. Account should be taken of a possible loss in weight of the crucible itself, if the blast is very powerful.

⁶ And 2 or 3 cc of bromine water. Bromine water is used for the purpose of collecting practically all the manganese here, instead of allowing it to distribute among several different precipitates.

⁷ This precipitate contains TiO_2 , P_2O_5 , Mn_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 ,⁸ 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 HF and H_2SO_4 .⁹ 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.¹⁰

The strength of the permanganate solution should not be greater than 0.0040 g Fe_2O_3 per cc.

LIME (CaO)

To the combined filtrate from the $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ precipitate a few drops of NH_4OH are added, and the solution brought to boiling. To the boiling solution 20 cc of a saturated solution of ammonium oxalate is 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 is burned off over a small flame of a Bunsen burner. It is then ignited, redissolved in HCl , and the solution made up to 100 cc 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,¹¹ weighed as oxide after ignition and blasted in a covered crucible to constant weight, or determined with dilute standard permanganate.¹²

MAGNESIA (MgO)

The combined filtrates from the calcium precipitates are acidified with HCl and concentrated on the steam bath to about 150 cc, 10 cc of saturated solution of $\text{Na}(\text{NH}_4)\text{HPO}_4$ is 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 orthophosphate begins to form, and then in moderate excess, the stirring being continued for

⁸ Or the corresponding pyrosulphates which are less troublesome and more effective than the acid sulphates.

⁹ This correction of Al_2O_3 , Fe_2O_3 for silica should not be made when the HF 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_2 are still to be found with the Al_2O_3 , Fe_2O_3 .

¹⁰ In this way only is the influence of titanium to be avoided and a correct result obtained for iron.

¹¹ The volume of wash water should not be too large; vide Hillebrand. *United States Geological Survey, Bull.* 122, p. 170.

¹² The accuracy of this method admits of criticism, but its convenience and rapidity demand its insertion.

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 cc, 1 cc of a saturated solution of $\text{Na}(\text{NH}_4)\text{HPO}_4$ 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,¹³ when it is filtered on a paper or a Gooch crucible, ignited, cooled, and weighed as $\text{Mg}_2\text{P}_2\text{O}_7$.

The pyrophosphate invariably contains calcium which can be determined as follows:

Dissolve the ignited pyrophosphate in a little dilute H_2SO_4 and add enough absolute alcohol to make about 90 to 95 per cent of the final volume. After several hours collect the small and sometimes almost invisible precipitate of calcium sulphate on a small filter and wash it free of phosphoric acid with alcohol. Dry the filter and extract from it the precipitate by a few cubic centimeters of hot water acidulated with HCl. Make this solution alkaline with ammonia, throw in a few crystals of ammonium oxalate and continue heating till a precipitate becomes visible. After an hour filter, wash, and ignite to calcium oxide. Its weight, averaging perhaps 0.5 mg is to be added to that of the lime already found and subtracted as tricalcium phosphate (not pyrophosphate) from that of the magnesium pyrophosphate.

In order to determine approximately the iron and aluminum present the following procedure may be followed:

Evaporate the alcoholic filtrate from the calcium sulphate and heat the residue to destroy separated organic matter. Take the residue up with a little HCl and water and when dissolved add a drop of bromine water. Add ammonia till the magnesia is again precipitated and let stand for an hour. Decant most of the supernatant liquid and add slowly, drop by drop, acetic acid till all fine-grained matter has dissolved. Usually there will remain a little flocculent matter which is likely to consist in greater part or wholly of phosphates of iron and aluminum (and manganese if this last was not removed by bromine and ammonia as in the section on Alumina and Iron Oxides). After ignition the precipitate often shows a reddish color. Unless great care is exercised this separation will lead to erroneous results, either by inclusion of magnesium with the impurities as weighed or by loss of these in consequence of using too much acetic acid.

ALKALIES (K_2O AND Na_2O)

For the determination of the alkalis, 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 .

SULPHURIC ANHYDRIDE ACID (SO_3)

One gram of the substance is dissolved in 15 cc (5 cc) of HCl, and 45 cc water, filtered, and the residue washed thoroughly.¹⁴

¹³ A paper filter should always be used if the pyrophosphate is to be corrected for contaminations.

¹⁴ Evaporation to dryness is unnecessary unless gelatinous silica should have separated, and should never be performed on a bath heated by gas; vide Hillebrand; *United States Geological Survey Bulletin* 422, p. 193.

The solution is made up to 250 cc in a beaker and boiled. To the boiling solution 10 cc of a saturated solution of BaCl_2 ¹⁵ 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 overnight, 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 cc with distilled water, boiled, the sulphur precipitated as BaSO_4 and allowed to stand overnight, or for a few hours.

The following procedure is in accordance with the recommendation of W. F. Hillebrand in United States Geological Survey, Bulletin 422, page 227:

In a platinum crucible mix 1 gram of the sample with one-half gram of sulphur-free sodium carbonate. Place the covered crucible in a hole in an asbestos board that is held in a somewhat inclined position and apply a blast flame upon the crucible below the asbestos for 10 to 15 minutes. Transfer the sintered mass to a beaker and cover with water. Cleanse the crucible with dilute hydrochloric acid and pour the solution into the beaker. Add more acid till decomposition is complete in the cold or on gently warming. Filter, wash with hot water, dilute to 150 to 200 cc, boil, and precipitate with barium chloride.

It should be borne in mind that by neither of the methods given is a barium sulphate obtained that is perfectly pure. Ferric (and if present alkali) sulphate, also barium chloride, contaminate it and it is impossible to correct for them directly. The most convenient way to obtain a correction is by a blank with a solution containing sulphur and the other main constituents of the cement in approximately the amounts and proportions found in the test sample.

LOSS ON IGNITION

Half a gram of cement is to be weighed out in a (covered) platinum crucible, placed in a hole in an asbestos board so that about three-fifths 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.

Recent investigations have shown that large errors in results are often due to the use of impure distilled water and reagents. The analyst should,

¹⁵ 10 per cent solution is preferable to one that is saturated.

therefore, test his distilled water by evaporation and his reagents by appropriate tests before proceeding with his work.

INSOLUBLE RESIDUE

The insoluble residue¹⁶ shall be determined on a 1-gram sample which is digested on the steam bath in hydrochloric acid of approximately 1.035 specific gravity until the cement is dissolved. The residue is filtered, washed with hot water, and the filter paper contents digested on the steam bath in a 5 per cent solution of sodium carbonate. The residue is then filtered, washed with hot water, then with hot hydrochloric acid, approximately of 1.035 specific gravity, and finally with hot water, then ignited and weighed. The quantity so obtained is the insoluble residue.

III. INTERPRETATION OF RESULTS

CHEMICAL

The composition of normal Portland cement has been the subject of a great deal of investigation and it can be said that the quantities of silica, alumina, oxide of iron, lime, magnesia, and sulphuric anhydride can vary within fairly wide limits without materially affecting the quality of the material.

A normal American Portland cement which meets the standard specifications for soundness, setting time and tensile strength has an approximate composition within the following limits:

	Per cent
Silica.....	19-25
Alumina.....	5-9
Iron oxide.....	2-4
Lime.....	60-64
Magnesia.....	1-4
Sulphur trioxide.....	1-1.75
Loss on ignition.....	0.5-3.00
Insoluble residue.....	0.1-1.00

It is also true that a number of cements have been made both here and abroad which have passed all standard physical tests in which these limits have been exceeded in one or more particulars, and it is equally true that a sound and satisfactory cement does not necessarily result from the above composition.

It is probable that further investigation will give a clearer understanding of the constitution of Portland cement, but at present chemical analysis furnishes but little indication of the quality of the material.

Defective cement usually results from imperfect manufacture, not from faulty composition. Cement made from very finely ground material, thoroughly mixed and properly burned, may be perfectly sound when

¹⁶ This determination was not considered by the Committee of the Society of Chemical Industry and is reproduced from paragraph 19 of the United States Government specification for Portland cement.

containing more than the usual quantity of lime, while a cement low in lime may be entirely unsound due to careless manufacture.

The analysis of a cement will show the uniformity in composition of the product from individual mills, but will furnish little or no indication of the quality of the material. Occasional analysis should, however, be made for record and to determine the quantity of sulphuric anhydride and magnesia present.

The ground clinker as it comes from the mill is usually quick setting which requires correction. This is usually accomplished by the addition of a small quantity of more or less hydrated calcium sulphate, either gypsum or plaster of Paris. Experience and practice have shown that an addition of 3 per cent or less is sufficient for the purpose.

Three per cent of calcium sulphate (CaSO_4) contains about 1.75 per cent sulphuric anhydride (SO_3), and as this has been considered the maximum quantity necessary to control time of set, the specification limits the SO_3 content to 1.75 per cent.

The specification prohibits the addition of any material subsequent to calcination except the 3 per cent of calcium sulphate permitted to regulate time of set. Other additions may be difficult or impossible to detect even by a careful mill inspection during the process of manufacture, but as the normal adulterant would be ground raw material, an excess of "insoluble residue" would reveal the addition of silicious material, and an excess in "loss on ignition" would point to the addition of calcareous material when either is added in sufficient quantity to make the adulteration profitable.

The effect of relatively small quantities of magnesia (MgO) in normal Portland cement, while still under investigation, can be considered harmless. Earlier investigators believed that as magnesia had a slower rate of hydration than lime, the hydration of any free magnesia (MgO) present would occur after the cement had set and cause disintegration.

The effect of magnesia was considered especially injurious when the cement was exposed to the action of sea water. More recent investigation has shown that cement can be made which is perfectly sound under all conditions when containing 5 per cent of magnesia and it has also been found that the lime in Portland cement exposed to sea water is replaced by magnesia.

The maximum limit for magnesia has been set at 4 per cent, as it has been established that this quantity is not injurious and it is high enough to permit the use of the large quantities of raw material available in most sections of the country.

PHYSICAL

Specific gravity.—If the Le Chatelier apparatus is used for the determination of specific gravity, the clean volumometer flask is filled with benzine free from water (which can be obtained by placing some calcium chloride or caustic lime in the benzine storage jar) to a point on the stem

between zero and 1 cubic centimeter. The flask is then placed in a constant temperature bath until volume is constant. The usual method is to introduce 64 grams of cement into the flask, taking care that the powder does not adhere to the tube above the liquid, and to free the cement from air by rolling the flask in an inclined position. The flask is then replaced in the constant temperature bath until a constant volume is recorded.

The specific gravity is obtained from the formula:

$$\text{specific gravity} = \frac{\text{weight of cement in grams}}{\text{displaced volume in cu. cm.}}$$

The specific gravity of a Portland cement is not an indication of its cementing value. It will vary with the constituents of the cement, especially with the content of iron oxide. Thus the white or very light Portland cements, containing only a fraction of a per cent of iron oxide, usually have a comparatively low specific gravity ranging from 3.05 to 3.15, while a cement containing 3 to 4 per cent or more of iron oxide may have a specific gravity of 3.20 or even higher. It is materially affected by the temperature and duration of burning the cement, the hard-burned cement having the higher specific gravity. A comparatively low specific gravity does not necessarily indicate that a cement is underburned or adulterated, as large percentages of raw materials could be added to a cement with a normally high specific gravity before the gravity would be reduced below 3.10.

If a Portland cement fresh from the mill normally has a comparatively low specific gravity, upon aging it may absorb sufficient moisture and carbon dioxide to reduce the gravity below 3.10. It has been found that this does not appreciably affect the cementing value of the material; in fact, many cements are unsound until they have been aged. Thus a re-determination is permitted upon a sample heated to a temperature sufficient to drive off any moisture which might be absorbed by the cement subsequent to manufacturing, but would not drive off any carbon dioxide nor correct underburning in the process of manufacturing the cement.

The value of the specific gravity determination lies in the fact that it is easily made in the field or laboratory, and when the normal specific gravity of the cement is known, any considerable variation in quality due to underburning or the addition of foreign materials may be detected.

Fineness.—Only the extremely fine powder of cement called flour possesses appreciable cementing qualities and the coarser particles are practically inert adding little to the cementing value for several weeks or months after mixing with water. No sieve is fine enough to determine the flour in a cement, nor is there any other means of accurately and practically measuring the flour. Some cements grind easier than others, thus, although a larger percentage of one cement may pass the 200-mesh sieve than another, the former may have a smaller percentage of actual flour due to the difference in the hardness and the character of the clinker, and the method used in grinding. Thus the cementing value of different cements can not be compared directly upon their apparent fineness through a 200-mesh sieve.

With cement from the same mill, with similar clinker and grinding machinery, however, it is probable that the greater the percentage which passes the 200-mesh sieve the greater the percentage of flour in that particular cement.

Normal Consistency.—The quantity of water used in making the paste from which the pats for soundness, tests of setting, and the briquettes are made, is very important and may vitally affect the results obtained. The determination consists in measuring the quantity of water required to bring a cement to a certain state of plasticity.

In determining the normal consistency by the ball method, after mixing the paste it should be formed into a ball with as little working as

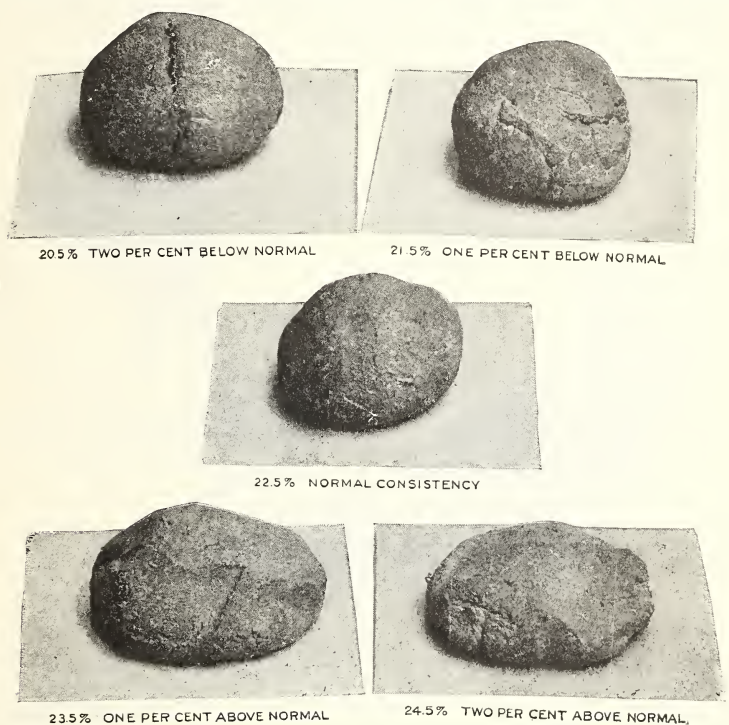


Fig. 1.—Appearance of Ball for Different Consistencies of Cement Paste

possible and a new batch of cement should be mixed for each trial paste. In order to obtain just the requisite quantity of paste to form a ball 2 inches in diameter, a measure made from a pipe with a 2-inch inside diameter cut $1\frac{1}{3}$ inches long will be found convenient. The section of pipe should be open at both ends, so that it can be pushed down onto the paste on the mixing table and the excess paste cut off with the trowel. The appearance of the ball using the correct percentage of water for normal consistency as compared with a less and greater quantity of water is shown in Fig. 1.

Mixing.—The homogeneity of the cement paste is dependent upon the thoroughness of the mixing, and this may have considerable influence upon the time of setting and the strength of the briquettes.

Soundness.—The purpose of this test is to detect those qualities in a cement which tend to destroy the strength and durability. Unsoundness is usually manifested by a change in volume which causes cracking, swelling, or disintegration. If the pat is not properly made, or if it is placed where it will be subject to any drying during the first 24 hours, it may develop what are known as shrinkage cracks, which are not an indication of unsoundness and should not be confused with disintegration cracks, as shown in Figs. 2 and 3. No shrinkage cracks should develop after the first 24 or 48 hours. The failure of the pats to remain on the glass nor the cracking of the glass to which the pat is attached does not necessarily indicate unsoundness. In molding the pats, the cement paste should first be flattened on

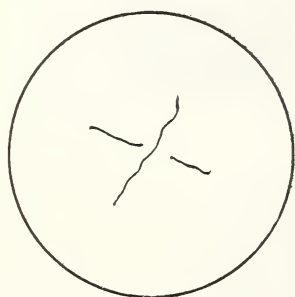


Fig. 2.—Soundness Pat Showing Shrinkage Cracks

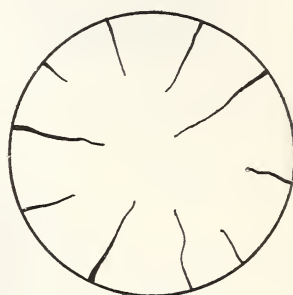


Fig. 3.—Soundness Pat Showing Disintegration Cracks

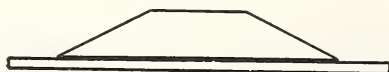


Fig. 5.—Soundness Pat with Top Surface Flattened for Determining Time of Setting

the glass and the pat formed by drawing the trowel from the outer edge toward the center, as shown in Fig. 4.

Time of Setting.—The purpose of this test is to determine the time which elapses from the moment water is added until the paste ceases to be plastic and the time required for it to obtain a certain degree of hardness. The determination of the "initial set" or when plasticity ceases is the more important, as a disturbance of the material after this time may cause a loss of strength and thus it is important that the mixing and molding or the incorporating of the material into the work be accomplished within this time. The time of setting is usually determined upon one of the pats which is to be used for the soundness test, the top surface being flattened somewhat, as shown in Fig. 5. In using the Gillmore needles care should be taken to apply the needles in a vertical position and perpendicular to the surface

of the pat. Fig. 6 shows an arrangement for mounting the Gillmore needles so that they are always perpendicular to the surface of the pat. The rate of setting and hardening may be materially affected by slight changes in temperature. The percentage of water used in gauging and the humidity of the moist closet in which the test pieces are stored may also affect the setting somewhat.

Tensile Tests.—Consistent results can only be obtained by exercising great care in molding and testing the briquettes. The correct method of filling the mold is shown in Figs. 7 and 8. In testing, the sides of the briquette and the clips should be thoroughly cleaned and free from grains of sand or dirt which would prevent a good bearing, and the briquette

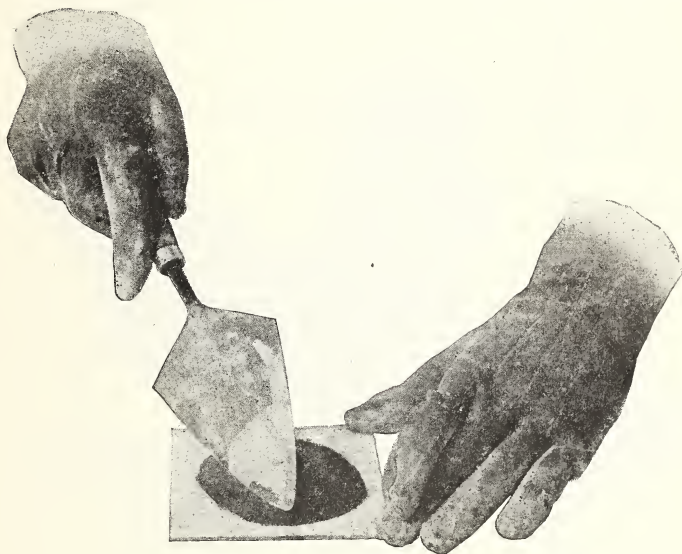


Fig. 4.—Correct Method of Molding Cement Pat

should be carefully centered in the clips so as to avoid cross strains. It may be considered good laboratory practice if the individual briquettes of any set do not show a greater variation from the mean value than 8 per cent for sand mixtures and 12 per cent for neat mixtures.

IV. AUXILIARY SPECIFICATIONS

BUREAU OF STANDARDS SIEVE SPECIFICATIONS

Wire cloth for standard sieves for cement and sand shall be woven (not twilled) from brass, bronze, or other suitable wire, and mounted on the frames without distortion.

The sieve frames shall be circular, about 20 centimeters (7.87 inches) in diameter, 6 centimeters (2.36 inches) high, and provided with a pan about 5 centimeters (1.97 inches) deep and a cover.

NO. 100 CEMENT SIEVE, 0.0055-INCH OPENING

The No. 100 sieve should have 100 wires per inch and shall conform to the following specifications of diameter of wire and size of mesh:

The diameter of the wires in the sieve should be 0.0045 inch and the average diameter of such wires as may be measured shall not be outside the limits 0.0042 to 0.0048 inch for either warp or shoot wires. The number of warp wires per whole inch, as measured at any point of the sieve, shall not

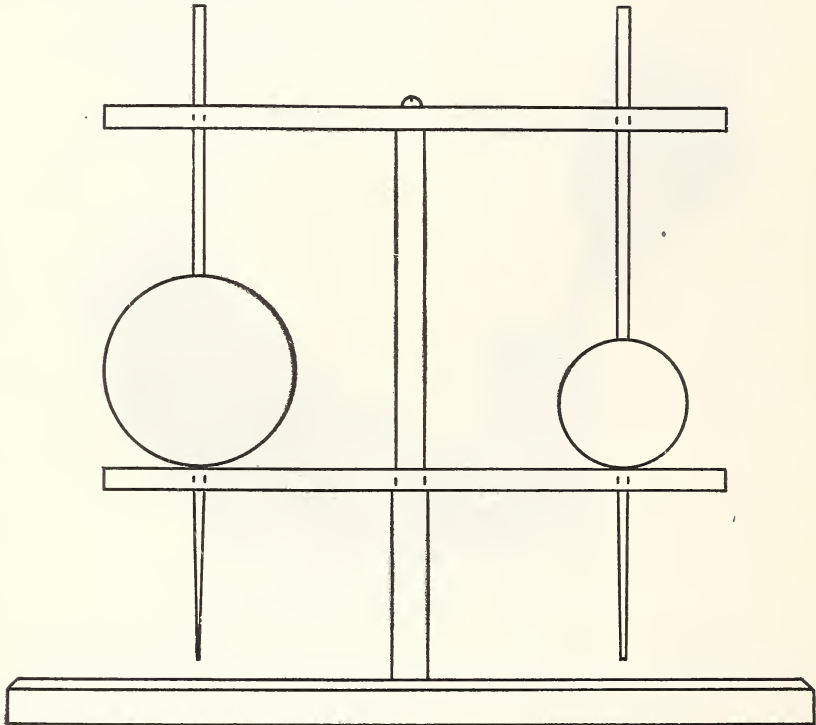


Fig. 6.—*Method of Mounting Gillmore Needles*

be outside the limits 98 to 101 per inch, and of the shoot-wires 96 to 102 per inch. For any interval of 0.25 to 0.50 inch in which the mesh may be measured the mesh shall not be outside the limits 95 to 101 wires per inch for the warp wires and 93 to 103 wires per inch for the shoot wires.

NO. 200 CEMENT SIEVE, 0.0029-INCH OPENING

The No. 200 sieve should have 200 wires per inch and shall conform to the following specifications of diameter of wire and size of mesh:

The diameter of the wires in the sieve should be 0.0021 inch, and the average diameter of such wires as may be measured shall not be outside the limits 0.0019 to 0.0023 inch for either warp or shoot wires. The number of warp wires per whole inch, as measured at any point of the sieve, shall not be outside the limits 195 to 202 per inch, and of the shoot wires 192 to 204 per inch. For any interval of 0.25 to 0.50 inch in which the mesh may be measured the mesh shall not be outside the limits 192 to 203 wires per inch for the warp wires and 190 to 205 wires per inch for the shoot wires.

NO. 20 SAND SIEVE, 0.0335-INCH OPENING

No. 20 sieves shall have between 19.5 and 20.5 wires per whole inch of the warp wires and between 19 and 21 wires per inch of the shoot wires.

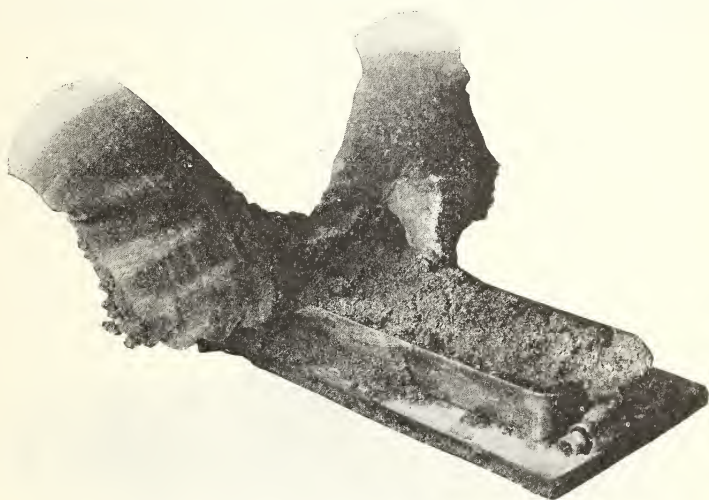


Fig. 7.—Correct Method of Filling Briquette Mold

The diameter of the wire should be 0.0165 inch and the average as measured shall not vary outside the limits 0.0160 to 0.0170 inch.

NO. 30 SAND SIEVE, 0.0223-INCH OPENING

No. 30 sieves shall have between 29.5 and 30.5 wires per whole inch of the warp wires and between 28.5 and 31.5 wires per whole inch of the shoot wires. The diameter of the wire should be 0.0110 inch and the average as measured shall not vary outside the limits 0.0105 to 0.0115 inch.

BUREAU OF STANDARDS SPECIFICATION FOR SPECIFIC-GRAVITY FLASKS

Material and Annealing.—The material from which the flasks are made shall be glass of the best quality, transparent, and free from striæ. It shall adequately resist chemical action and have small thermal hysteresis. The

flasks shall be thoroughly annealed at 400°C to 500°C for 24 hours and allowed to cool slowly before being graduated. They shall be of sufficient thickness to insure reasonable resistance to breakage.

Design.—The cross section of the flask shall be circular and the shape and dimensions shall conform to the diagram shown in Fig. 9. This design is intended to insure complete drainage of the flask on emptying and stability of standing on a level surface, as well as accuracy and precision of reading. The neck of the flask shall be cylindrical for at least 1 centimeter above and below every graduation mark. There shall be a space of at least 1 centimeter between the highest graduation mark and the lowest point of the grinding for the glass stopper.

Capacity.—The flask should contain approximately 250 cc when filled to the zero graduation mark.

Graduations.—The neck shall be graduated from 0 to 1 cc and from



Fig. 8.—*Correct Method of Troweling Surface of Briquettes*

18 cc to 24 cc into 0.1-cc divisions. The 0.1-cc graduations should be continued two below the 0 and two above the 1-cc graduation. The graduations shall be of uniform width, finely but distinctly etched, and shall be perpendicular to the axis of the flask. The 0.1-cc graduations shall be at least 1 millimeter apart. This will require an internal diameter of the neck not greater than 11.3 millimeters. The 1-cc graduations shall extend completely around the neck of the flask and shall be numbered to indicate the capacity. The 0.1-cc graduations shall extend at least halfway around the neck and the 0.5-cc graduations shall have a length about midway

between the other two. The graduation marks shall have no apparent irregularities of spacing.

Standard Temperature.—The flasks shall be standard at 20° C. The

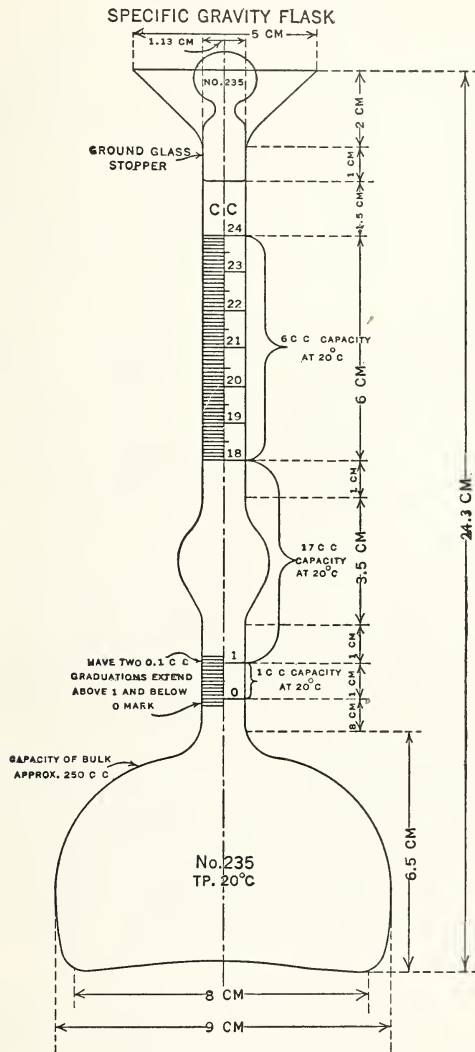


Fig. 9.—Diagram Showing Form and Dimensions of Specific-Gravity Flask

indicated specific gravities will then be at 20° referred to water at 4° as unity—that is, density at 20° in grams per cc.

Inscriptions.—Each flask shall bear a permanent identification number and the stopper shall bear the same number. The standard temperature

shall be indicated and the unit of capacity shall be shown by the letters "cc" placed above the highest graduation mark.

Tolerance.—The error of any indicated capacity shall not be greater than 0.05 cc.

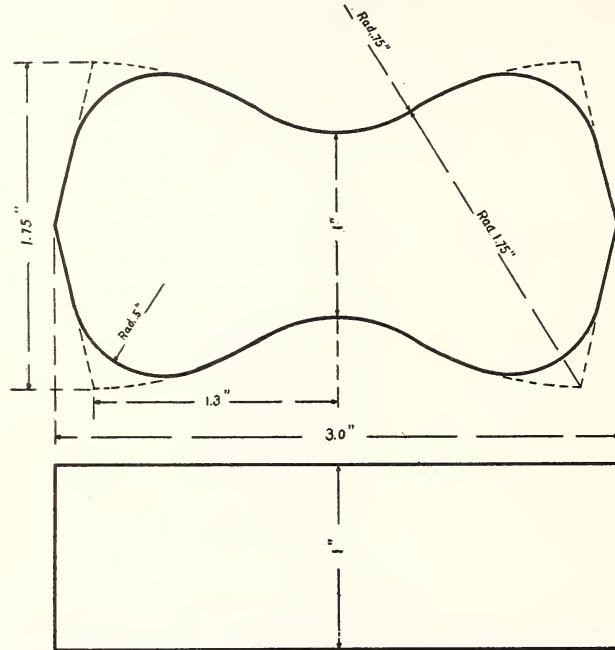


Fig. 10.—Form of Briquette as Recommended by the Committee on Uniform Tests of Cement of the American Society of Civil Engineers

Interpretation of Specification.—The foregoing specification is intended to represent the most desirable form of specific-gravity flask for use in testing cements. Variations of a few millimeters in such dimensions as total height of flask, diameter of base, etc., are to be expected and will not be considered sufficient cause for rejection. The specification in regard to tolerance, inscriptions, length, spacing, and uniformity of graduations will, however, be rigidly enforced.