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THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

BY THOS. B. STILLMAN, PH.D.

THE enlarged consumption of Portland cement in this country during the past few years has caused the subject of its chemical and physical properties to receive increased consideration. Not only has the consumer been directly interested, that the cements used should stand specified tests, but the attention of the manufacturer has been drawn in the same direction, resulting in improvements in methods of production.

While the Portland cement manufacture here is yet in its infancy, with a history of practically less than ten years, its product for 1891 reached a total of 450,000 barrels out of 3,500,000 barrels consumed in this country during that year. This ratio between home production and importation should be radically changed in the near future, since the product for 1892 was over 600,000 barrels. A number of causes have prevented the use of American Portland cements in the home market, one of the chief being that the imported German cements always gave higher physical tests when made by the German methods of testing than the American cements under the American system of testing. There are a number of American Port-

land cements fully as good as the best German cements, and have shown fully as high tensile strength when tested by the same methods.

These differences in results are not due entirely to the cements, but rather to the methods in use in the different countries for testing them, for Portland cements cannot vary much in their chemical composition without losing their value.

The limit of variation is as follows:

CaO	58	to 67	per cent.[1]
SiO_2	20	to 26	"
Al_2O_3	5	to 10	"
Fe_2O_3	2	to 6	"
MgO	0.5	to 3	"
SO_3	0.5	to 2	"

After manufacture it is practically Ca_3SiO_5, and is quite distinct from another product made and largely consumed here called "hydraulic cement."

Experience has shown that Portland cements containing over two per cent. of magnesia (MgO) are inferior in lasting qualities, and by the gradual absorption of water produce cracking and disintegration (*Compt. Rend.*, May, 1886).

Calcium carbonate ($CaCO_3$), formed by the absorption of CO_2 by the CaO in the cement after manufacture, is another injurious compound found in cements containing more CaO than sufficient to unite with the silica to form the tri-silicate of lime. This carbonate of lime gradually produces seams and fractures after the setting of the cement. The "Ecole Nationale," of Paris, rejects all cements containing over 1.5 per cent. of sulphuric acid. Thus, if upon chemical analysis, magnesia is found present in amount over two per cent., carbonic and sulphuric acids in amounts over one and one-half per cent., *the cement can be condemned at once without any mechanical tests.* Therefore, it is evident that a careful test of a Portland cement requires: (1) a chemical analysis to determine the proportion of the ingredients and (2) the mechanical or physical tests to determine fineness, tensile strength, and resistance to crushing.

[1] E. Candlot, *Étude pratique sur le Ciment de Portland* (Paris, 1886).

Weigh out 2 gms. of the finely powdered and dried material, transfer to a 6-inch porcelain capsule, add 50 cc. HCl, 5 cc. HNO_3, and evaporate to dryness; add 25 cc. HCl, 100 cc. H_2O, boil and filter into a ¼ liter flask; wash well; make solution up to containing mark and thoroughly mix.

(1) *Residue.*—Dry, ignite, fuse in platinum crucible with Na_2CO_3; cool, dissolve in water, acidify with HCl, evaporate to dryness in 4-inch porcelain capsule; take up with HCl and water; boil, filter and wash.

(2) *Solution* [1].—Take 1 sample of 100 cc., transfer to a 300 cc. beaker, make alkaline with NH_4OH, warm, filter, and wash.

(3) *Residue*, Fe_2O_3, Al_2O_3. Dry, ignite and weigh as such. Then fuse in silver dish with KHO. Treat with water, boil, and filter.

(4) *Solution.*—Add ammonium oxalate in slight excess, set aside 4 hours, filter, wash with water containing ¼ its bulk of ammonium hydrate.

(5) *Residue* is CaC_2O_4. Dry, ignite over blast-lamp to constant weight. Weigh as CaO.

(6) *Solution.*—Evaporate to dryness in a platinum capsule, ignite to expel all ammonia salts; cool, add 50 cc. H_2O, boil, filter and wash.

(7) *Residue* is MgO. Dry, ignite and weigh as Mgo.

(8) *Solution.*—Transfer to a weighed platinum capsule, add a few drops of H_2SO_4 and evaporate to dryness; ignite to constant weight. This weight represents Na_2SO_4, K_2SO_4, $MgSO_4$. Dissolve in 50 cc. of H_2O, mix well and divide into 2 portions of 25 cc. each.

1st Portion.—Add a few drops of HCl, then make alkaline with NH_4OH, and precipitate the Mg with solution of Na_2HPO_4. Set aside 3 hours, filter, wash with ammoniated water, dry, ignite and weigh as $Mg_2P_2O_7$, and calculate to $(MgSO_4)_2$. This weight, multiplied by 2, is subtracted from weight of total sulphates in (8). Calculate $MgSO_4$ to MgO.

2d Portion.—Add solution of $PtCl_4$ in slight excess, a few drops of HCl and evaporate to dryness on the water-bath. Determine weight of K_2PtCl_6 on tared filters and calculate to K_2SO_4. Multiply this by 2 and subtract weight from total sulphates. The weights of K_2SO_4 and $MgSO_4$ subtracted from total sulphates gives the remainder as Na_2SO_4. Calculate K_2SO_4 to K_2O. Calculate Na_2SO_4 to Na_2O.

Residue, SiO_2. Dry, ignite and weigh as SiO_2.

Solution.—Make alkaline with NH_4OH; warm, filter, wash. (Neglect filtrate.) Residue is Al_2O_3. Dry, ignite, and weigh as Al_2O_3.

Residue, Fe_2O_3. Dry, ignite, and weigh as Fe_2O_3. Subtract this weight from weight in (3). The difference is Al_2O_3.

Solution, contains Al_2O_3. If it is desired to weigh this acidify the solution with HCl, then make faintly alkaline with NH_4OH; boil, filter, wash well. The precipitate is dried, ignited and weighed as Al_2O_3.

SO₃.—50 cc. of the solution are transferred to a 100 cc. beaker; solution of $BaCl_2$ is added in slight excess; boil and set aside for 6 hours; filter, wash, dry, ignite and weigh as $BaSO_4$, and calculate to SO_3.

$$\text{wt. of } SiO_2 \times 100 = \%\ SiO_2.$$
$$\text{Crucible} + \tfrac{1}{2}\ SiO_2 = 11.205 \text{ gms.}$$
$$\text{Crucible} = 10.721 \text{ "}$$
$$SiO_2 = 0.484$$
$$\frac{0.484 \times 100}{2} = 24.26\%\ SiO_2.$$

SiO_2.

$$\frac{\text{wt. } Al_2O_3 \times 100}{2} = \%\ Al_2O_3.$$
$$\text{Crucible} + \tfrac{1}{2}\ Al_2O_3 = 10.743 \text{ gms.}$$
$$\text{Crucible} = 10.721 \text{ "}$$
$$Al_2O_3 = 0.022 \text{ "}$$
$$\frac{0.022 \times 100}{2} = 1.10\%\ Al_2O_3.$$

Al_2O_3.

$$\text{wt. of } Fe_2O_3 \times 2.5 \times 100 = \%\ Fe_2O_3.$$
$$\text{Crucible} + \tfrac{1}{2}\ Fe_2O_3 = 10.745 \text{ gms.}$$
$$\text{Crucible} = 10.721 \text{ "}$$
$$Fe_2O_3 = 0.024 \text{ "}$$
$$\frac{0.024 \times 2.5 \times 100}{2} = 3.00\%\ Fe_2O_3.$$

Fe_2O_3.

$$\text{wt. of } Al_2O_3 \times 2.5 \times 100 = \%\ Al_2O_3.$$
$$\text{Crucible} + \tfrac{1}{2}\ Al_2O_3 = 10.762 \text{ gms.}$$
$$\text{Crucible} = 10.721 \text{ "}$$
$$Al_2O_3 = 0.041 \text{ "}$$
$$\frac{0.041 \times 2.5 \times 100}{2} = 5.12\%\ Al_2O_3.$$

Al_2O_3.

$$\text{wt. } CaO \times 2.5 \times 100 = \%\ CaO.$$
$$\text{Crucible} + \tfrac{1}{2}\ CaO = 11.2223 \text{ gms.}$$
$$\text{Crucible} = 10.7210 \text{ "}$$
$$CaO = 0.5013 \text{ "}$$
$$\frac{0.5013 \times 2.50 \times 100}{2} = 62.67\%\ CaO.$$

Cao.

$$\text{Crucible} + MgO = 10.725 \text{ gms.}$$
$$\text{Crucible} = 10.721 \text{ "}$$
$$MgO = 0.004 \text{ "}$$
$$MgO \text{ from (8)} = 0.0058 \text{ "}$$
$$0.0098 \text{ "}$$
$$\frac{0.0098 \times 2.5 \times 100}{2} = 1.22\%\ MgO.$$

MgO.

Alkaline sulphates K_2SO_4, Na_2SO_4, $MgSO_4$ + platinum dish, 33.8050 gms.
Platinum dish, 33.7550 "
Total sulphates, 0.0500 "

$$\text{Crucible} + Mg_2P_2O_7 = 10.729 \text{ gms.}$$
$$\text{Crucible} = 10.721 \text{ "}$$
$$Mg_2P_2O_7 = 0.008 \text{ "} = 0.0088\ MgSO_4 \times 2 = 0.0176\ (MgSO_4)$$
$$0.0324\ (K_2SO_4, Na_2SO_4)$$
$$K_2PtCl_6 = 0.0232 = 0.0082\ K_2SO_4 \times 2 = 0.0164\ (K_2SO_4)$$
$$0.0160\ (Na_2SO_4)$$

$0.0176\ MgSO_4 = 0.0058\ MgO$ and is added to MgO in (7)

$0.0164\ K_2SO_4 = 0.0088\ K_2O$, then $\frac{0.0088 \times 2.5 \times 100}{2} = 1.10\%\ K_2O$

$0.0160\ Na_2SO_4 = 0.0069\ Na_2O$, then $\frac{0.0069 \times 2.5 \times 100}{2} = 0.86\%\ Na_2O$

K_2O. **Na_2O.**

$$\text{Crucible} + BaSO_4 = 10.729$$
$$\text{Crucible} = 10.721$$
$$BaSO_4 = 0.008$$
$$SO_3 = 0.0027$$
$$\frac{0.0027 \times 5 \times 100}{2} = 0.67\%\ SO_3.$$

SO_3.

[1] Manganese oxide is seldom found in Portland cement. If qualitative analysis has indicated its presence, the iron oxide and alumina must be separated out by sodium acetate process in (2) of above scheme. The filtrate containing the manganese is treated with bromine, the MnO_2 filtered off, and the filtrate treated as directed in (4).

RÉSUMÉ.

	Per cent.
SiO_2	24.20
Al_2O_3	6.22
Fe_2O_3	3.00
CaO	62.67
MgO	1.22
K_2O	1.10
Na_2O	0.86
SO_3	0.67
Total	99.94

The following well known brands of Portland cements were analyzed in my laboratory by above method.

	Burham's.	Dyckerhoff's.	Saylor's.
SiO_2	21.70 per cent.	19.05 per cent.	21.25 per cent.
Al_2O_3	6.82 "	7.90 "	4.21 "
Fe_2O_3	2.37 "	5.38 "	8.25 "
CaO	62.26 "	63.62 "	61.25 "
MgO	1.48 "	1.87 "	1.50 "
K_2O	1.84 "	0.88 "	1.01 "
Na_2O	0.98 "	0.36 "	0.99 "
SO_3	1.20 "	0.94 "	1.38 "
CO_2	1.30 "	....	....
	99.95 "	100.00 "	99.84 "

In some cements quartz is a constituent in amounts varying from 0.5 to 6 per cent. It can be separated from combined silica by the method of Fresenius (*Quant. Chem. Anal.*, p. 259).

Where carbonic acid has been indicated by the qualitative analysis the quantitative analysis should be made upon at least eight grams of the cement.

The carbonic acid rarely reaches one per cent., and while it is generally absent in well-burned cements, it is by no means an uncommon constituent to the amount of 0.15–0.30 per cent., as the following table of analyses of German cements will show[1]:

	1	2	3	4	5	6	7	8
CaO	61.99	62.89	63.71	63.27	65.59	59.96	64.51	60.81
SiO_2	23.69	22.80	25.37	19.80	22.85	23.70	22.38	22.63
Fe_2O_3	2.71	3.40	3.14	3.22	2.76	3.15	2.24	2.42
Al_2O_3	8.29	7.70	4.31	6.73	5.51	8.20	9.45	7.06
MgO	0.47	1.20	1.25	2.02	1.24	1.00	....	2.89
Alkalies	0.95	1.30	0.84	1.48	0.92	1.05	....	2.83
SO_3	0.69	0.71	0.87	1.08	1.69	0.88	1.44	0.47
CO_2	0.27	....	....	0.23	....	0.26	....	0.33
Insoluble	0.44	....	....	1.38	....	0.80	....	....

[1] *Der Portland-cement und seine Anwendungen im Bauwesen*, Berlin, 1892, p. 18.

THE MECHANICAL TESTING.

The method recommended for use in this country by the American Society of Civil Engineers is as follows:

(1) Determination of fineness.

(2) Liability to checking or cracking.

(3) Tensile strength.

Fineness.—Tests should be made upon cements that have passed through a No. 100 sieve (10,000 meshes to the square inch), made of No. 40 wire, Stubb's wire gauge. The finer the cement the more sand it will unite with and the greater its value.

Liability to Checking or Cracking.—Make two cakes of neat cement two or three inches in diameter, about one-half inch thick, with thin edges. Note the time in minutes that these cakes, when mixed with mortar to the consistency of a stiff, plastic mortar, take to set hard enough to stand the wire test recommended by General Gillmore, one-twelfth inch diameter wire loaded with one-fourth pound, and one twenty-fourth inch diameter wire loaded with one pound.

One of these cakes, when hard enough, should be put in water and examined from day to day to see if it becomes contorted or if cracks show themselves at the edges, such contortions or cracks indicating that the cement is unfit for use at that time. In some cases the tendency to crack, if caused by too much lime, will disappear with age. The remaining cake should be kept in the air and its color observed, which, for a good cement, should be uniform throughout.

Tensile Strength.—One part of the cement mixed with three parts of sand for the seven days and upward test, in addition to the trials of the neat cement. The proportions of cement, sand, and water should be carefully determined by weight, the sand and cement mixed dry, and all the water added at once. The mixing must be rapid and thorough, and the mortar, which should be stiff and plastic, should be firmly pressed into the molds with the trowel without ramming and struck off level, the molds in each instance, while being charged and manipulated, to be laid directly on glass, slate, or other non-absorbent material. The molding must be completed before incipient

setting begins. As soon as the briquettes are hard enough to bear it, they should be taken from the molds and kept covered with a damp cloth until they are immersed. For the sake of uniformity, the briquettes, both of neat cement and those containing sand, should be immersed in water at the end of twenty-four hours, except in the case of one day tests. Ordinary clean water having a temperature between 60° F. and 70° F. should be used for the water of mixture and immersion of sample. The proportion of water required is approximately as follows:

For briquettes of neat cement, about twenty-five per cent.

For briquettes of one part cement, one part sand, about fifteen per cent. of total weight of cement and sand.

For briquettes one part cement, three parts sand, about twelve per cent. of total weight of cement and sand.

The object is to produce the plasticity of rather stiff plasterer's cement.

An average of five briquettes may be made for each test, only those breaking at the smallest section to be taken. The briquettes should always be put in the testing machine and broken immediately after being taken out of the water, and the temperature of the briquettes and of the testing room should be constant between 60° F. and 70° F.

The following table shows the average minimum and maximum tensile strength per square inch which some good cements have attained. Within the limits given the value of a cement varies closely with the tensile strength when tested with the full dose of sand.

AMERICAN AND FOREIGN PORTLAND CEMENTS.—NEAT.

1 Day (1 hour, or until set, in air, the rest of the 24 hours in water)..
.....from 100 to 140 lbs. per square inch
1 Week (1 day in air, 6 days in water)..from 250 to 550 lbs. per square inch
1 Month, 28 days (1 day in air, 27 days in water).....
.....from 350 to 700 lbs. per square inch
1 Year (1 day in air, the remainder in water) .....
.....from 450 to 800 lbs. per square inch

AMERICAN AND FOREIGN PORTLAND CEMENTS.—1 PART OF CEMENT TO 3 PARTS OF SAND.

1 Week (1 day in air, 6 days in water..from 80 to 125 lbs. per square inch
1 Month, 28 days (1 day in air, 27 days in water).....
.....from 100 to 200 lbs. per square inch

1 Year (1 day in air, the remainder in water).....
.... from 200 to 350 lbs.[1] per square inch

The machines for determining the tensile strength of Portland cements in use in this country are the "Fairbanks," Fig. 1, and the "Riehle," Fig. 2.

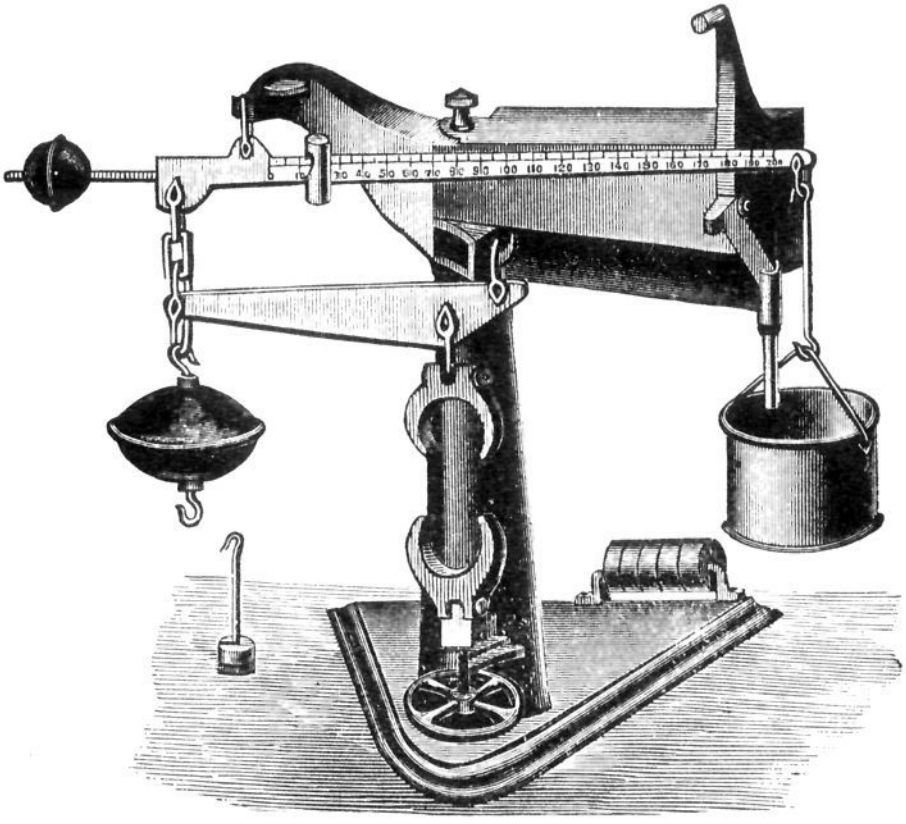


FIG. 1.

The Fairbanks machine is automatic and is operated as follows:

Hang the cup on the end of the beam; see that the poise is at the zero mark and balance the beam by turning the ball. Place the shot in the hopper. Place the briquette in the clamps and adjust the hand wheel so that the graduated beam will be inclined upward about 45°. Open the automatic valve so as to allow the shot to run slowly. When the specimen breaks the beam drops and closes the valve through which the shot has been pouring. Remove the cup with the shot in it and hang the counterpoise weight in its place. Hang the cup on the

[1] In regard to modification of these conditions required for tensile strength, consult *Transactions American Society of Civil Engineers*, August 1891, p. 285.

hook under the large balance ball and proceed to weigh the shot, using the poise on the graduated beam, and the weights on the counterpoise weight. The result will show the number of pounds required to break the specimen.

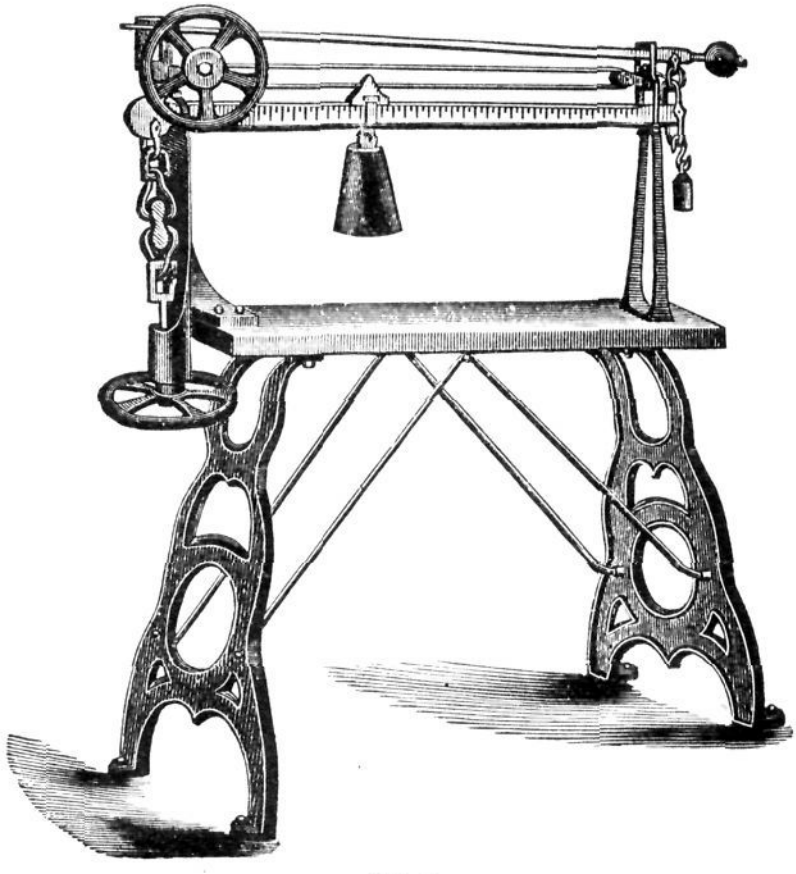


FIG. 2.

The "Riehle," while not automatic, is accurate, and responds to differences as slight as 1 pound in 2,000. The distinctive features are:

(*a*) The poise moves quietly and smoothly on the weighing beam.

(*b*) The weighing beam is long and the marks not too close together. The slightest movement of the beam is promptly and plainly observed by the motion of the indicator.

(*c*) The levers are tested and sealed to U. S. standard weight.

(*d*) The arrangement of the "grips" to hold the briquettes is such that they are always swung from pins, thus giving the test upon the cement when the briquette is on a dead straight line.

Directions for Testing Portland Cement According to the Official German Rules[1].—The quality of a mortar made with cement depends not only on the strength of the cement itself, but also on the degree of sub-division of the same. It is therefore necessary to make the tests both with neat cement and with a mixture of the same with "standard sand." This latter as used at the Royal Testing Station at Berlin, is produced by washing and drying quartz sand, which must be clean as possible, and afterwards be sifted through a sieve of sixty meshes per square centimeter (387 meshes per square inch), by which process the coarsest particles are separated. The sand is again sifted through a sieve having 120 meshes to the square centimeter (774 meshes per square inch). The residue remaining in this sieve is the standard sand for experiments, the coarsest and finest particles having been eliminated. It is absolutely necessary in order to obtain uniform results to use only the "standard sand," as the size of the grain has a material influence on the results of the testing. The sand must be clean and dry, and all earthy and other substances previously removed by washing.

Preparation of Briquettes of Neat Portland Cement.—Upon a slab of metal or marble are laid five sheets of filtering paper, which have been previously saturated with water, and upon these are placed five brass molds (Fig. 3) thoroughly clean and moistened with water. One thousand grams of cement and 250 grams of water must be thoroughly mixed, well worked up, and when the resulting mass has been rendered perfectly homogenous, it is poured into the molds. The latter must be gently tapped by means of a wooden hammer with equal force on both sides during ten to fifteen minutes to insure the escape of confined globules of air. The molds must be carefully filled up until the mass becomes plastic, the superfluous mortar is then struck off, and the mold carefully withdrawn. The samples, after remaining twenty-four hours exposed to the air, at a temperature of about 60° F., must be immersed in water having the same temperature, and care must be taken that they remain covered with water until the

Fig. 3.

[1] *Portland Cement*, by Gustav Grawitz.

time arrives for breaking them. In order to obtain a proper average at least ten briquettes should be prepared for every examination.

Preparation of Briquettes from a Mixture of Portland Cement and Standard Sand.—Place the molds on metal as described in preparation of neat cement briquettes. The quantities (by weight) specified of cement and sand are thoroughly mixed and to this is added the requisite quantity of water. The whole mass is then worked up with a trowel or spatula until it becomes uniform. In this manner is obtained a very stiff mortar. The

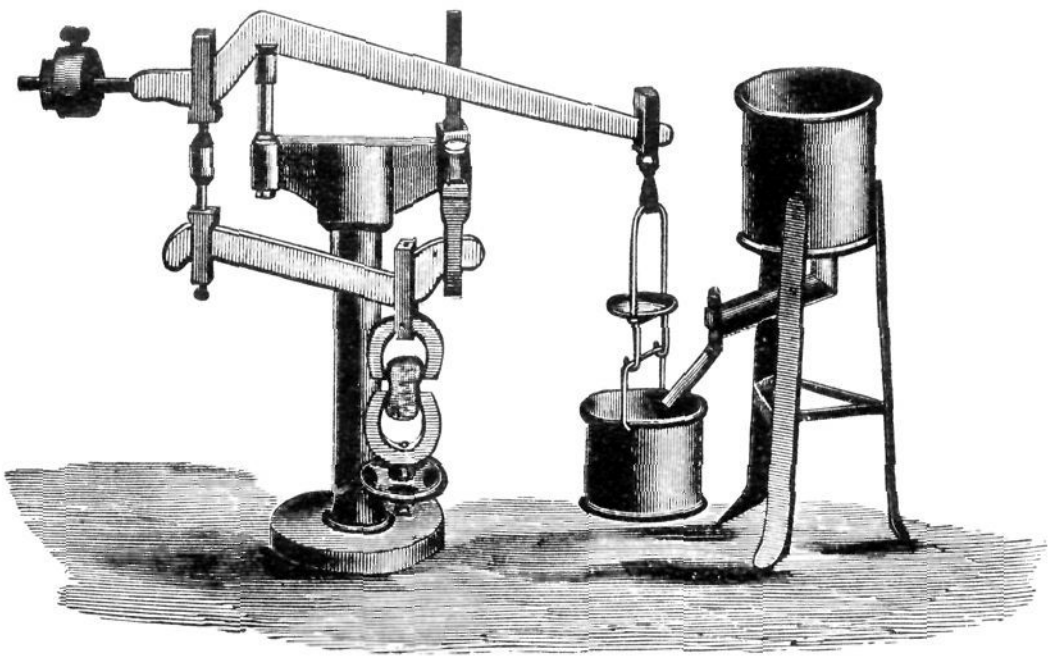


FIG. 4.

molds are filled and mortar heaped up. The latter is then beaten into the molds with an iron trowel, at first lightly, and afterwards more heavily, until it becomes elastic and water appears on the surface. The superfluous mortar is then scraped off with a knife and by means of the same the surface is leveled. The further treatment of these briquettes is the same as for neat cement briquettes. The average of ten breaking weights furnishes the strength of the mortar tested.

The machine in general use in Germany for determining the tensile strength of cements is the Michaelis (Fig. 4), and from

this is derived, with modifications, the "Reid and Bailey" machine in use in England, and the "Fairbanks" previously described.

[TO BE CONTINUED.]

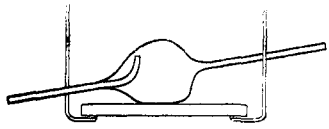
A NEW WEIGHING APPARATUS.

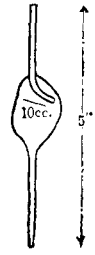
BY DR. H. SCHWEITZER.

Read before the New York Section May 29, 1893.

THE weighing of liquids for analytical purposes has always been very tedious, and many forms of apparatus have been devised for facilitating this operation. But all of them had disadvantages. The distinguishing feature of our "Weighing Pipette," which was constructed with the help of our assistant, Mr. E. Lungwitz, is that it consists of a single piece without any cock or other complicated parts.

The weighing pipette presents the general appearance of a bulb pipette. Where the suction tube joins the bulb there is a short capillary tube which projects towards the wall of the bulb, the opposite wall being flattened to furnish a firm rest for the pipette on the scale. Our pipettes are constructed with either large or small apertures of the delivery tube, according to the physical properties of the substance to be weighed. For light liquids, acids, and oils we use small apertures; for milk, syrups, heavy oils, and fats we take pipettes with large apertures.





By capillarity and suction the liquid runs back into the delivery tube without any losses. For example, we weighed a quantity of fuming sulphuric acid in a pipette with small aperture, and after half an hour no change in the weight of the pipette was perceptible. A short delivery tube cannot be used as there is danger of the liquids running back on the outside of the tube, thereby dripping on the scales.