This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

Examination of Portland Cement

THE

Chemical and Physical Examination

OF

Portland Cement

BY

RICHARD K. MEADE, B.S.,
Instructor in Chemistry in Lafayette College

EASTON, PA.:
THE CHEMICAL PUBLISHING COMPANY.
1901.

PREFACE

In the preparation of this little manual, the author has drawn largely for advice upon his friends and others engaged in the cement industry who were kind enough to give him help, and it is to thank these that he has prefixed this note. Aside from this, it may not be amiss to say here that this book is the outcome of the author's interest in the rapidly growing Portland cement industry in America. The methods both of chemical analysis and physical examination have been explained with, what may seem to the experienced chemist, useless detail, but it must be remembered that many of the cement manufacturing companies are employing young men fresh from technical schools, whose college training may be excellent, but whose laboratory experience upon work of this kind is usually limited to a few analyses. Probably the greater number of young cement chemists are required to make physical tests without having had any training whatever in the subject. It is for these, as well as the young engineer and the student of chemistry and engineering, that the notes and explanations have been added to the methods. The author wishes to acknowledge his indebtedness to Prof. J. Madison Porter, C.E., of Lafayette College, and to Dr. P. W. Shimer, of Easton, Pa., for their kind help. Professor Porter read the section upon the physical testing of cement and added much to its value by his suggestions for its improvement. Others who have kindly aided the author are: Messrs. Andreas Lundteigen, chemist, Western Portland Cement Co., Yankton, S. D.; Julian O. Hargrove, assistant inspector of asphalt and cements, District of Columbia; Thos. A. Hicks, chemist, Art Portland Cement Co., Sandusky, O.; S. B. Newberry, manager Sandusky Portland Cement Co., O.; J. G. Bergquist, superintendent cement department, Illinois Steel Co., Chicago; J. Dunraven Young, analytical chemist, Chicago; Willett C. Pierson, chemist, Glens Falls Portland Cement Co., N. Y.; and A. C. Ferguson, C.E., St. Louis Water Works Department.

LAFAYETTE COLLEGE, EASTON, PA., June, 1901.

CONTENTS

INTRODUCTION.

ANALYTICAL METHODS.

PHYSICAL METHODS.

DETECTION OF ADULTERATION IN PORTLAND CEMENT.

APPENDIX.

INTRODUCTION

The Nature and Composition of Portland Cement and Current Theories of its Hardening

Definition.

Portland cement is a product resulting from the heating to incipient fusion of a mechanical mixture of limestone and clay, or similar materials containing silica, lime and alumina, and then grinding finely the resulting clinker.[1] When the fine powder is mixed with water chemical action takes place, and a hard mass is formed. The change undergone by the cement mortar in passing from the plastic to the solid state is termed "setting." This usually requires but a few hours at most. On completion of the set a gradual increase in cohesive strength is experienced by the mass for some time, and the cement is said to "harden." Cements usually require from six months to a year to gain their full strength. Cement differs from lime in that it hardens while wet and does not depend upon the carbon dioxid of the air for its hardening. It is very insoluble in water and is adapted to use in moist places or under water where lime mortar would be useless. Below is a table showing the analysis of various Portland cements.

[1] German standard rules.

ANALYSIS OF VARIOUS PORTLAND CEMENTS

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O K_2O	SO_3	CO_2	H_2O
1	23.30	5.85	4.65	60.90	0.90	0.30	2.43	1.40	
2	22.04	7.35	4.14	61.94	0.91	0.59	1.38	1.65	
3	19.55	10.65	3.30	59.55	2.41	0.88	2.08	1.40	
4	27.74	7.74	3.70	56.68	0.57	0.63	1.66*	6.28	
5	27.18	8.85	....	59.50	1.41	....	0.99	....	
6	25.60	6.13	3.47	60.19	0.70	....	1.13	2.70	
7	22.20	6.72	2.28	67.31	0.95	....	0.26	0.40	
8	26.00	6.65	2.75	61.60	1.08	....	0.84	1.10	
9	22.63	7.06	2.42	60.81	2.89	2.83	0.47	0.33	....
10	22.85	5.51	2.76	65.59	1.24	0.92	1.69	....	....
11	20.80	7 39	2.61	64.00	....	....	....	....	
12	23.48	9.42		62.92	1.20	0.90	1.25	trace	0.31† 0.17‡
13	22.89	8.00	2.44	63.38	2.30	....	....	0.99	
14	23.36	8.07	4.83	58.93	1.00	0.50	0.85*	2.46	

1. English Portland, made from chalk and Thames estuary mud.
2. English Portland, made from chalk and clay found at Hull.
3. English Portland, made from clay and alkali waste.
4. English Portland, given by Reid as first quality.
5. Belgian Portland.
6. Belgian Portland.
7. French Portland.
8. French Portland.
9. German Portland.
10. German Portland.

* Calcium sulfate. † Combined. ‡ Moisture.

11. American Portland cement, made of marl and blue clay.
12. American Portland, made from clay and marl.
13. American Portland, made from argillaceous limestone.
14. American Portland, made from argillaceous limestone.

Composition of Cement.

Portland cement, according to Le Chatelier,[1] consists of a mixture of tricalcium silicate, $3CaO.SiO_2$, and tricalcium aluminate, $3CaO.Al_2O_3$. He arrived at this conclusion after a long series of experiments, which consisted in examining thin sections of cement clinker under the polarizing microscope. He also made experiments upon the synthetic production of calcium silicates and aluminates by heating intimate mixtures of finely pulverized silica, alumina, and lime. He then examined into the hydraulic properties of the compounds so prepared. He, however, failed to prepare the tricalcium silicate directly by heating lime and silica, the result of the attempt being a mixture of lower silicates and lime, but gave it as his opinion that this compound could be prepared indirectly by heating together a mixture of fusible silicates and lime.

The tricalcium silicate is the essential element of Portland cement, in which it occurs in cubical crystals. In this compound the lime and silica bear the ratio of 168:60.4 or 2.78:1. From an analysis of Tiel "Grappiers" made by Hauenschild,[2] it will be seen that they are approximately pure tricalcium silicate.

---

[1] Annales des Mines, 1887, p. 345.

[2] Thonindustrie Zeitung, 1883, p. 418.

ANALYSIS OF TIEL "GRAPPIERS"

	Per cent.
Silica	23.6
Lime	64.7
Alumina	1.4
Ferric oxid	0.8
Magnesia	1.4
Sulfuric anhydrid	0.5
Water	7.6
	100.0
Ratio of lime to silica	2.74 : 1

Theory of the Hardening of Cement.

Le Chatelier also examined thin sections of hardened cement under the microscope and found that it consisted of hexagonal plates of crystallized calcium hydroxid, $Ca(OH)_2$, embedded in a white matrix of interlaced needle-shaped crystals of hydrated monocalcium silicate, $(CaSiO_3)_2.5H_2O$. From these researches he concluded that the tricalcium silicate when mixed with water reacts to form a hydrated monocalcium silicate and calcium hydroxid according to the reaction,

$$2Ca_3SiO_5 + 9H_2O = (CaSiO_3)_2.5H_2O + 4Ca(OH)_2.$$

The calcium hydroxid then probably reacts further upon the calcium aluminate of the cement, forming hydrated basic calcium aluminate, $Ca_4Al_2O_7.12H_2O$.

$$Ca_3Al_2O_6 + Ca(OH)_2 + 11H_2O = Ca_4Al_2O_7.12H_2O$$

The "hardening" of cements is due to the first reaction, but the formation of the hydrated basic calcium aluminate probably exerts a marked influence upon the "setting" properties of the cement.

Hydraulic Index.

Assuming that three molecules of lime are united to one of silica to form the tricalcium silicate, that three molecules of lime are united to one of alumina to form the tricalcium aluminate, and that these two compounds are the essential ingredients of cement, Le Chatelier gives the following as the ratio between the lime and magnesia, the basic elements, and the silica and alumina, the acid elements in a good cement

$$\frac{CaO + MgO}{SiO_2 + Al_2O_3} \leqq 3 \qquad (1)$$

and

$$\frac{CaO + MgO}{SiO_2 - Al_2O_3 - Fe_2O_3} \geqq 3. \qquad (2)$$

Le Chatelier also states that (1) usually gives for a good cement from 2.5 to 2.7, and (2) from 3.5 to 4.

This ratio between the silica and alumina on the one hand and the lime on the other is termed "*hydraulic index*."

Erdmenger[1] has pointed out, however, that the above equations are not borne out by experience, as the assumption that lime and magnesia are of equal hydraulic value is an error.

Messrs. Spencer B. and W. B. Newberry,[1] in a series of researches as to the constitution of cement, arrived at con-

---

[1] J. Soc. Chem. Ind., 11, 1035.

clusions quite different from those of Le Chatelier. They prepared silicates and aluminates of lime synthetically by heating together in a Fletcher gas furnace intimate mixtures of finely pulverized quatrz and calcium carbonate, and alumina and calcium carbonate in different molecular proportions. They then examined into the hardening and setting properties of the resulting compounds. While these chemists agreed with Le Chatelier that the silica in cement is present as tricalcium silicate, and that to this is due the ultimate hardening of cement, they found no difficulty in preparing the tricalcium silicate directly, by heating together silica and lime in the molecular proportion of 1 to 3. The Messrs. Newberry, however, from their experiments upon the calcium aluminates concluded that the alumina is in combination with the lime as dicalcium aluminate and not as tricalcium aluminate. Their experiments led them to the following conclusions:

Messrs. Newberrys' Theories.

"*First.*—Lime may be combined with silica in the proportion of 3 molecules to 1, and still give a product of practically constant volume and good hardening properties, though hardening very slowly. With 3½ molecules of lime to 1 of silica the product is not sound, and cracks in water.

"*Second.*—Lime may be combined with alumina in the proportion of 2 molecules to 1, giving a product which sets quickly, but shows constant volume and good hardening

---

[1] J. Soc. Chem. Ind., 1897, p. 889.

properties. With 2½ molecules of lime to 1 of alumina the product is not sound."

Newberry's Formula.

The formula for the tricalcium silicate, $3CaO.SiO_2$, corresponds to 2.8 parts by weight of lime to 1 part of silica, and the formula for the dicalcium aluminate, $2CaO.Al_2O_3$, corresponds to 1.1 parts of lime to 1 of alumina. From this the following formula is given as representing the maximum of lime which should be present in a correctly balanced Portland cement: per cent lime = per cent silica × 2.8 + per cent alumina × 1.1.

They found that cement prepared synthetically with lime, alumina, and silica proportioned according to the above formula gave good results, whereas that prepared by Le Chatelier's formula was unsound, showing the lime to be in excess.

Substances Found in Cement.

From this it will be seen that the essential ingredients of Portland cement are lime, silica, and alumina. A little of the alumina is always replaced by ferric oxid, and some of the lime by magnesia. Small percentages of alkalies, potash and soda, present in the clay as silicates, are also in cement, while the most thorough burning fails to drive off all the carbon dioxid from the limestone or marl in the raw mixture, leaving a trace in the finished product. This trace is increased by the absorption of the constituent from the atmosphere. Coal contains sulfur; this when burned becomes sulfur dioxid, a gas which is absorbed by the uncombined lime of the cement mixture, or left in the ash when it unites with lime to form calcium sulfate. Some sulfur also enters the cement from the clay or marl. These are the chemical constituents for which cements are mainly analyzed. Usually it is sufficient to know the silica, lime, alumina and ferric oxid together, and the magnesia; less often the alumina and ferric oxid separately, the sulfuric acid and the carbon dioxid; while more rarely yet the alkalies, combined water, and the sulfur present as sulfate and sulfid respectively.

Lime.

A good cement contains from 58 to 67 per cent lime, the amount depending upon the relative proportions of silica and alumina, and also upon the care with which the cement has been manufactured. Up to the limit, it may be said, that the more lime that is present in a cement the greater will be its strength. The limit is reached, however, when more lime is present than will combine chemically with the silica and alumina, leaving some lime in the uncombined state, or, as Newberry's formula puts it, when the percentage of lime is greater than the percentage of silica multiplied by 2.8, plus the percentage of alumina multiplied by 1.1. Lime in slaking expands so that an excess of lime over what will unite with the silica and alumina will cause the cement to expand, or "blow" as it is technically termed, and crack.

If the lime is much under the limit, the cement will contain clay in excess, for the lime will not be present in sufficient quantity to change all the clay to silicates and aluminates. This excess of clay, of course, is devoid of cementing qualities and may be looked upon as just so much foreign matter. Though it will not cause the cement to fall to pieces subsequently, it takes away from its strength because in its place should be cement. The amount of lime a cement will bear depends upon the care with which the mixture of raw materials is made. Thus poorly ground, imperfectly mixed raw materials would probably result in a very much over-limed cement, if the lime limit (as shown by chemical analysis of the clay, marl, limestone or cement rock of the mixture) was anywhere near reached; for the coarse particles of calcium carbonate would not come into sufficiently close contact with the silica and alumina to completely combine with the latter. A properly burned cement will also stand a greater percentage of lime than an improperly burned one. A cement in which the temperature at burning was too low to heat all the lime to the point of combination with the silica and alumina, would naturally contain free lime. Chemical analysis, therefore, if taken alone as the guide to a cement, will seldom tell us much, where the lime content is concerned; as of two cements containing the same quantity of lime, one properly made might be quite sound while the other, from faulty mixing and burning, might be anything but sound. A method of determining the uncombined lime in cement would enable us to tell whether a given cement is sound or not, but unfortunately no method of accurately determining this constituent is now known, so that the physical test of mixing the cement with water and watching it for cracks, has to be resorted to as a test for free lime and soundness.

Alumina.

Portland cement usually contains between 5 and 10 per cent alumina. As the percentage of alumina rises, the cement becomes more quick-setting. When the percentage of alumina rises above 10 per cent the cement becomes very quick-setting, with a corresponding decrease of tensile strength. This is to be expected, since the strength of cement is due to the calcium silicate, and its setting properties to the calcium aluminate. As the calcium aluminate is very fusible, the clinkers obtained on burning mixtures high in alumina are very fusible, hard to burn uniformly and difficult to grind. Cement clinkers made from kaolin show all of these properties and the finished cement is low in tensile strength.

Ferric Oxid.

According to Le Chatelier, ferric oxid and calcium carbonate on burning yield products which slake with water and possess no hydraulic properties. Schott, however, prepared cement containing only lime, silica and ferric oxid, which showed excellent hardening qualities, and therefore concluded that alumina could be completely replaced by ferric oxid without diminishing in any way the hydraulic properties of cement. S. B. and W. B. Newberry from their researches concluded that ferric oxid and alumina act in a similar manner in promoting the combination of silica and lime. The amount of ferric oxid in cements is usually small, less than 5 per cent, and it is generally agreed that when not in excess of 5 or 6 per cent ferric oxid does not perceptibly effect the constructive value of cement. The dark gray color of cement is due to the presence of iron compounds. Cement prepared from silica, lime, and alumina only is colorless, but upon replacing the alumina by ferric oxid the cement becomes gray.

Magnesia.

A cement containing 1½ per cent of magnesia was long considered dangerous; now 3 per cent in cement is thought to be harmless, and many authorities allow even 5 per cent magnesia. The popular supposition is that magnesia in considerable percentages causes cement in time to expand and crack. R. Dykerhoff presented to the German Association of Cement Manufacturers in 1895 the results of a very thorough research into the effects of magnesia. From his experiments he concluded that magnesia, whether added to a normal mixture or substituted for an equivalent portion of lime, causes a decrease of strength in the resulting cement, when present in more than 4 per cent. Cracking only occurred with 8 per cent or more magnesia. A commission from the above association is now studying the effects of magnesia. Le Chatelier in his formula considers magnesia to replace lime, while the Newberrys in their formula consider it inactive and not to replace lime. The latter is probably the correct supposition.

Potash and soda are present in all cements in small quantities varying from 0.5 to 2.5 per cent. Cements made from the lime waste of alkali works often contain over this amount. Butler[1] states that instances have occurred in which these cements gave anything but satisfactory results, and the only fault that could be found with their chemical composition was a slight excess of alkali. In most cement the alkalies are present in such small quantity that their effects are of little importance. The old theory was that the presence of the alkalies promoted the combination of the lime with the silica and alumina. This does not seem to be borne out by experiments, however, and the presence of the alkalies is not now looked upon as essential to the formation of cement.

Alkalies.

Several compounds of sulfur are present in cement; chief of these are calcium sulfate and calcium sulfid. The action of calcium sulfate upon cement is to delay the set. For this reason it is often added in the form of gypsum to the cement after burning. The Association of German Cement Manufacturers so far recognize the beneficial effect of the addition as to allow manufacturers to employ a proportion not exceeding 2 per cent in order to confer to the cement, slow-setting properties. Although the presence of calcium sulfate in small quantities is beneficial to cement, there is no doubt that a quantity exceeding 4 or 5 per cent is injurious. The French

Sulfur.

---

[1] "Portland Cement," by D. B. Butler, p. 263.

[2] German Standard Rules.

specifications[1] exclude all cements which contain over 1 per cent sulfuric acid, but most engineers in this country in their specifications, if they mention it at all, allow 2 per cent of sulfur trioxid,[2] SO_3.

Calcium sulfid is objectionable in cement from the fact that it reacts with the iron compounds of the cement, forming iron sulfid. This latter absorbs oxygen from the air, forming iron sulfate, and this reaction causes expansion and disintegration.

Carbon Dioxid.

Carbon dioxid is present in all cements. If present in appreciable quantity it shows either a poorly burned cement; that is, one in which the heating was not carried to the point of driving out all the carbon dioxid from the calcium carbonate, or else a cement containing free lime, which has absorbed this constituent from the air. As natural cements are lighter burned than Portlands they contain a much larger percentage of carbon dioxid, as the table given below will show.

---

[1] French Government specifications.

[2] Specifications for municipal work in St. Louis, Mo.

ANALYSIS OF NATURAL CEMENTS

Made by Julian O. Hargrove, Asst. Inspector of Asphalts and Cements, Washington, D. C.

Brand.	SiO_2. Per cent.	Al_2O_3. Per cent.	Fe_2O_3. Per cent.	CaO. Per cent.	MgO. Per cent.	CO_2. Per cent.
Cumberland	29.92	11.23	4.78	36.50	11.63	5.42
Cumberland & Potomac	28.30	10.00	4.56	49.60	3 76	3.01
Lawrenceville	29.00	10.40	2.90	32.41	19.92	5.29
Potomac	28.44	9.68	4.28	36.06	16.04	4.75
Round Top	28.36	10.42	4.15	45.14	3.82	4.02

NOTE.—A very complete presentation of the more tenable views regarding the composition and hardening of cements will be found in an article "Ueber die Untersuchung und das Verhalten von Cement" by Dr. R. Zsigmondy in Dingler's polytechniches Journal, **294**, 89, 114, 137, 163.

ANALYTICAL METHODS

THE ANALYSIS OF CEMENT

Preparation of the Sample

The knowledge usually sought by a chemical analysis of cement is the average composition of a given lot or bin.

Sampling. In order that it shall give this, it is necessary that the small sample used in the analysis shall fairly represent the whole quantity, possibly many tons. In a large lot of cement, it is hardly probable that a small sample, or even a large sample, taken from one place in the bin or one barrel in the consignment, will have the average composition of the cement, since this particular point in the bin, or this special barrel, might be better or worse than the remainder. It is well in sampling from a bin to take small samples from various points, not merely upon the surface where the cement may have become slightly damaged by exposure to air or damp, but also underneath by using a fairly long brass tube. This latter should be slipped over a stick turned to fit the tube and having a sharp end. When thrust deep enough into the pile, the stick should be withdrawn from the tube and this then pushed a little farther into the pile. The cement in the end of the tube when withdrawn will furnish the sample. In sampling shipments it is best to take a sample from ten or more bags or barrels in each one hundred tons going for it well down into the heart of the bag or barrel, and not at the mouth. The samples may then be placed in a clean paper bag, labeled and taken to the laboratory, where they should be well mixed, and the bulk reduced to laboratory dimensions by halving down. To do this, pour the sample upon a piece of clean paper, mix well and divide the pile into quarters with a spatula. Brush away two of the diagonally opposite quarters with a small 1½-inch flat brush. Mix thoroughly the remaining two quarters and divide as before. Repeat this until the sample is reduced sufficiently. The final sample is now ground to the proper fineness, and if to be preserved, placed in a stoppered bottle and kept in a dark place. If for immediate use, a sample or coin envelope may be substituted for the bottle.

Often the chemist receives his sample from that sent the engineer in charge of the physical testing laboratory. In this case the mixing should have been already done and the bulk is small, so that only the grinding has to be done.

Grinding.

In order that the solvents and fluxes used in decomposing the cement for analysis may do their work thoroughly, it is necessary that the final sample be in the condition of a fine powder, free from any grit or hard particles. Cement is already ground more or less to such an impalpable state. Cement of the better grades is now pulverized so finely that only from 5 to 10 per cent is rejected by a sieve of 2,500 meshes per square inch.

Still the sample should be freed from all grit before weighing the portions to be used for the various determinations. Unless a very complete analysis has to be made, from 5 to 6 grams of cement are placed in an agate mortar, a little at a time, according to the size of the mortar and ground until no grit remains, as ascertained by rubbing between the fingers, or on the back of the hand, or biting with the teeth. When alkalies, combined water, etc., are to be determined or check analyses are to be run, it will probably be necessary to grind a larger quantity than 6 grams. From the size and shape of the ordinary agate mortar and pestle the operation of grinding is very fatiguing. It may be much facilitated, however, by cutting a hole, of such size and shape as to hold the mortar firmly, in the middle of a block of hard wood, a foot or so square. The pestle is then fixed in a piece of round brass tubing of sufficient bore, or else in a round hard wood handle. Several mechanical grinders are on the market, descriptions of which may be found in the trade catalogues of most of the prominent dealers in chemical apparatus.

Drying.

The finely ground sample will now contain more or less hygroscopic moisture. This should be gotten rid of by spreading the sample upon a watch-glass in an oven and drying for one hour at a temperature of from 100°–110° C. It is then removed, poured into a clean dry test-tube while still hot, and tightly corked; or the cement may be placed in the test-tube instead of the watch-glass and thus dried.

Instead of drying the sample some analysts prefer to determine the moisture and report the amount found in their analysis. To do the latter, place 1 gram of the sample in a previously weighed platinum or porcelain crucible, a watch-glass, or a weighing tube. Take the weight of the whole and dry in an oven at 105°–110° C. for one hour, or until no further loss in weight occurs. Weigh again; the loss represents moisture.

Any of the three forms of oven described below will be found useful for drying cement samples, precipitates, etc. The first two can be purchased from dealers and the third can easily be made from "scraps" around the laboratory.

The ordinary steam oven is made of copper, doubly cased throughout with the exception of the door. The casing is filled at its opening to about three-fourths of its height with water and heat applied by a Bunsen burner underneath. When the water boils, the upper part of the casing becomes full of steam and the temperature of the oven approaches 100° C. Unless provided with an arrangement for maintaining a "constant water-level," they require watching in order to prevent the boiling off of the water.

When a temperature above 100° C. is required, the air-bath must supplant the steam oven. The construction is similar to that of the latter, except that the casing is single. Air-baths are usually provided with false bottoms of sheet iron in order to prevent the destruction of the real one of copper by the burner flame. It is necessary to control the temperature of the air-bath, however, by a thermometer inserted through a cork, in the opening, in the top of the oven. The required temperature can be maintained by adjusting the stop-cock of the gas supply. After the gas has once been regulated the temperature will remain constant for some hours. Gas regulators, called "thermostats," can be purchased from dealers in chemists' supplies, and while they are liable to become clogged and get out of order, they still are very convenient for keeping a constant temperature.

The author recently described (in the *Scientific American*, vol. lxxx, p. 230) a form of drying oven which he has used successfully in his laboratory for some years. It is non-corrosive, simple and cheap. In the metal ovens, the acid fumes, given off in "baking" certain substances, attack the metal, forming a scale which, in spite of care, will sooner or later drop in some sample or dish drying in the oven. Fig. 1 shows the oven. Select a large glass bottle and cut off the bottom by making a mark on it with a file, wrapping two strips of wet paper, one a little above and one a little below the mark, and revolving the bottle slowly and evenly while the tip of a small blowpipe flame or small flame from a blast-lamp plays on the space be-

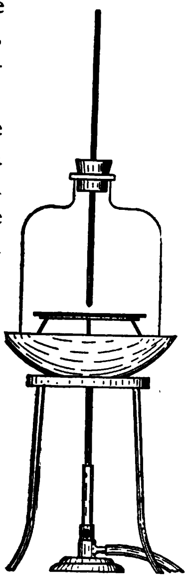

Fig. 1.

tween the paper. A crack will start in a few moments, which will follow the flame around the bottle. The sharp edges should be smoothed by a file dipped in turpentine, and a narrow strip of asbestos wound around the neck for a handle. The upper half of the bottle is placed upon a sand-bath or hot plate, and the object to be heated, upon a support of glass or porcelain, raised above the sand-bath by a wire bent to form a tripod. The temperature is regulated by a thermometer thrust through a cork in the mouth of the bottle. Large grooves should be cut lengthwise along the cork to make a free escape for the steam and vapors, and to create a current of hot air through the oven. Both this and the other form of air-bath described should be set in a corner shielded from air drafts. If this is done the maintaining of a constant temperature will be much simplified.

Determination of Silica, Ferric Oxid and Alumina, Lime and Magnesia

Notes on the Decomposition of Cement.

The chemical elements which go to make up limestones, cements, and clays are the same, varying only in proportions and state of combination, yet these differences are such that while limestones are decomposed by quite dilute hydrochloric acid, clays are practically unacted upon by that acid even when concentrated. Analytically cements lie on the one side between limestones and marls, which are easily decomposed by dilute hydrochloric acid, and on the other, clays and refractory silicates requiring for decomposition fusion with alkaline carbonates.

If a limestone is treated with hydrochloric acid of 1.07 sp. gr. the decomposition will be practically complete and the small amount of silica usually found in limestones, when separated by evaporation, will be found nearly free from impurities. If, however, the percentage of silica is high, the impurities rise greatly; especially is this the case when the limestone also contains much alumina. With Portland cement acid of this strength fails to bring about complete decomposition and the silica resulting from the treatment will be much less pure than that from a limestone. If, however, the strength of the acid is increased to about 1.10 sp. gr., the decomposition of the cement is nearly complete and in a freshly burned Portland cement the percentage of the other constituents left with the silica is so small as to be hardly worth accounting for in a technical analysis. Fusion of either the sample directly, or the impure silica obtained by treatment with acid of the strength last indicated, with sodium carbonate or a mixture of sodium and potassium carbonates undoubtedly gives much more accurate results. Still where rapid analyses are required, especially at the cement mill itself, where the analysis of freshly burned cement is usually that desired, the decomposition by means of dilute hydrochloric acid (1 to 1) is usually employed, and it gives results which are sufficiently near the truth for checking the quality of the product. In analyzing unknown brands of cement, or cement which has stood for some time, or where great accuracy is desired, it is best to use one of the methods depending upon the decomposition by ignition or fusion with alkaline carbonates, thus insuring a complete breaking up of the silicates.

When calcium and magnesium are precipitated, as oxalate and phosphate respectively, from solutions containing much sodium or potassium salts, the precipitates are almost sure to be contaminated with alkaline salts. Even much washing fails to remove the impurity from the precipitate. When, therefore, the sample of cement has been fused directly with from 5 to 10 grams of sodium carbonate, there is sure to be this danger that the lime and magnesia precipitates will carry down some sodium salts, from which subsequent washing will fail to free them. In accurate work this error can be eliminated by reprecipitation. If instead of fusing the sample directly with five to eight times its weight of sodium carbonate, the impure silica, separated by treatment with hydrochloric acid, is fused with an equal bulk of sodium carbonate, the quantity of sodium salts introduced into the solution will be reduced to one-fourth, usually between 1.0 and 1.5 gram of sodium chlorid.

To save reprecipitation of the lime and magnesia, and at the same time break up the silicates, Dr. Porter W. Shimer, of Lafayette College, has devised a method depending upon a fact which he discovered, that ignition with sodium carbonate even in the proportion of 1 gram of cement to 0.5 gram of sodium carbonate serves completely to break up the silicates. The quantity of sodium salts introduced into the solution from 0.5 gram of carbonate is so small that possible contamination of the lime and magnesia precipitates is done away with. On heating cement and sodium carbonate together in this proportion no fusion takes place, only a sintering. This method is given first of the four as the author believes it to be best for general use. Where technical requirements demand rapidity the method of solution in hydrochloric acid without fusion will be found satisfactory.

By Ignition of the Sample with Sodium Carbonate

Silica.

Weigh 1 gram of the finely ground dried cement into a platinum crucible and mix intimately by stirring with a glass rod with 0.5 gram of pure dry sodium carbonate. Brush off the rod into the crucible with a camel's hair brush. Cover the crucible and place over a low flame. Gradually raise the flame until the crucible is red hot and continue the heating for five minutes longer; the nplace over a blast-lamp and heat five minutes more. While still hot, plunge the bottom of the crucible half the way up into cold water. This will loosen the mass. Drop the mass into a casserole or dish and cover the latter with a watch-glass. Pour into the crucible a portion of a mixture of 30 cc. of hot water and 10 cc. of dilute hydrochloric acid. Heat on a hot plate, and then pour into the dish or casserole. Clean out the crucible with a rubber-tipped rod, using the rest of the mixture of acid and water. To the solution in the casserole add a few drops of concentrated nitric acid and evaporate to dryness on a hot plate or water-bath, using care to prevent spattering. Heat the dry mass until all odor of hydrochloric acid has disappeared. This can be done safest in the oven described on page 19 at 110° C. Add 15 cc. of dilute hydrochloric acid to the contents of the dish and digest a few moments, then dilute to 50 cc. with hot water, filter and wash well with hot water. Dry the precipitated silica by placing paper and residue in a previously weighed crucible, and setting over a low flame. Ignite and weigh as silica, SiO_2. Calculate the percentage and report as such.

Ferric Oxid and Alumina

Heat the filtrate from the silica to boiling, add ammonia in slight but distinct excess, boil five minutes, allow to settle, filter in a beaker capable of holding 1 liter, and wash the precipitate a few times with hot water. Redissolve the precipitate in hydrochloric acid by pouring the acid around the edges of the paper and stirring up the precipitate with a jet of water from a wash-bottle. Allow the solution to run into the beaker in which the precipitation was made. Wash the paper well with cold water. Bring the hydrochloric acid solution to boiling, add ammonia in slight but distinct excess and filter. Allow the filtrate to run into that from the first precipitation. Wash the precipitate well with hot water, dry, ignite, and weigh as ferric oxid and alumina. To determine separately the Fe_2O_3 and the Al_2O_3, refer to "Determination of Ferric Oxid" and subtract the percentage of ferric oxid found from the combined percentage of ferric oxid and alumina; the difference will be the alumina, Al_2O_3.

Lime.

Dilute the combined filtrates to about 800 cc., if not already so, bring to a boil, make strongly ammoniacal, and add 25 cc. of a saturated solution of ammonium oxalate. Stir a little and let stand one hour. Filter, wash well with hot water, dry and ignite, first over a Bunsen burner until all the carbon is burned off, and then over a blast-lamp for fifteen minutes. Cool and weigh. Again heat for five minutes over a blast-lamp and weigh. Repeat, if necessary, until the weight is constant, that is, two weights agree to within 0.0002 gram of each other. The ignition has changed the precipitate to calcium oxid, CaO. Weigh as such and calculate the percentage.

Magnesia.

Concentrate the filtrate somewhat by evaporation after acidifying slightly with hydrochloric acid, and adding 20 cc. of sodium phosphate. Set the solution in a vessel of water to cool, and then add, drop by drop, from a burette, with constant stirring, ammonia until slightly ammoniacal and the precipitate begins to appear. Stop adding ammonia, stir for five minutes, add one-tenth the volume of the liquid of strong ammonia and stir for three minutes. Allow the solution to set in a cool place over night, filter in the morning, and wash well with a mixture of 1 liter water, 500 cc. ammonia (0.96 sp. gr.), and 150 grams ammonium nitrate. Dry, ignite, and weigh as magnesium pyrophosphate, $Mg_2P_2O_7$, which multiplied by 0.36190 gives the equivalent of magnesia, MgO.

By Solution of the Sample in HCl and Fusion of the Insoluble Residue with Na_2CO_3

Silica.

Weigh 1 gram of finely ground dried cement into a 5 inch casserole, add 30 cc. of hydrochloric acid (sp. gr. 1.10) and 2 cc. of nitric acid. Evaporate to dryness and heat at 110° C. until all smell of hydrochloric acid is gone. Add 15 cc. dilute hydrochloric acid and 100 cc. water, heat to boiling and filter. Ignite the residue upon the filter in a platinum crucible until all the carbonaceous matter of the paper is burned, fuse with 1.5 gram of sodium carbonate, first over a Bunsen burner, and then over a blast-lamp, until the contents of the crucible are in quiet fusion. Remove the crucible from the flame and run the fused mass well up on the sides of the crucible by tilting and revolving the latter while held with the crucible tongs. While still hot plunge the crucible three-quarters of the way into clean cold water, which will frequently cause the mass to loosen from the sides of the crucible. Wash off any of the material spattered on the crucible cover into a casserole with hot water, and add the fused mass in the crucible if it has come loose. If not, fill the crucible with hot water and digest on the hot plate until the fused mass softens and can be removed to the casserole. Clean the crucible with water, dissolving in dilute hydrochloric acid any particles adhering too firmly to the crucible to be removed from it by gentle rubbing with a rubber-tipped rod. When the hot water has thoroughly disintegrated the fusion, cover the casserole with a watch-glass and strongly acidify the contents with hydrochloric acid. Heat until effervescence ceases and everything dissolves except silica. Wash off the watch-glass and evaporate the solution to dryness. Heat for one hour at 110° C., or until all odor of hydrochloric acid has disappeared, add 100 cc. hydrochloric acid and 50 cc. water, warm until all soluble salts are in solution, filter, wash well with hot water, dry, ignite, and weigh as silica, SiO_2.

Ferric Oxid, Alumina, Lime, and Magnesia.

Mix the two filtrates from the silica separations and proceed to determine iron and alumina, lime and magnesia, as directed in the foregoing method. A much better way, however, would be not to mix the two filtrates, but to precipitate the iron, alumina, lime, and magnesia in each filtrate separately, as the precipitate of calcium oxalate is almost sure to carry down some sodium salts. If desired, the precipitates of a kind may be ignited together in the same crucible. The author adopts, when using this method, the plan of holding back the main filtrate (that from the impure silica) and dissolving the precipitate from the second filtrate (that from the pure silica) in a little dilute hydrochloric acid after washing once or twice with water, and adding it to the main filtrate just before making the corresponding precipitation in the main filtrate. For example, the slight precipitate of iron and alumina obtained on adding ammonia to the second filtrate from the silica, would be dissolved in hydrochloric acid and the solution added to the main filtrate before adding ammonia to the latter to precipitate the main body of the ferric oxid and alumina.

Some chemists merely determine the iron and alumina in the filtrate from the silica by fusion, disregarding any calcium and magnesium which might have been carried down with the impure silica, as inappreciable. Dr. Shimer has shown[1] that this quantity is not so small, and hence it is advisable to determine also the lime and magnesia in the second filtrate.

By Fusion of the Sample Itself with Sodium Carbonate[2]

Silica. Weigh 1 gram of the finely ground cement and mix with about 6 grams of dry sodium carbonate; transfer to a platinum crucible and fuse, first at a low heat, then for about twenty minutes in the flame of the blast lamp. After fusion cool the crucible and place in a beaker with 50 cc. of hot water and 20 cc. of strong hydrochloric acid. Cover the beaker with a watch-glass, place on a steam-bath, and allow to remain until the fused mass has completely dissolved. Remove the watch-glass and crucible, rinsing both with hot water, add a few drops of nitric acid, and evaporate the contents of the crucible to dryness;

---

[1] J. Am. Chem. Soc., 21, 289.

[2] Method as used by Julian O. Hargrove, Assistant Inspector of Asphalts and Cements of the District of Columbia.

moisten the residue with a few drops of hydrochloric acid and again evaporate to dryness. Place the beaker in an air-bath and heat at a temperature of 110° C. until all odor of acid has disappeared. Add 15 cc. dilute hydrochloric acid and 30 cc. hot water; after standing a few minutes filter through a weighed Gooch crucible into a 200 cc. graduated flask, wash with hot water, dry, ignite, and weigh as silica, SiO_2.

Dilute the filtrate in the graduated flask to the 200 cc. mark. Remove 100 cc. (with a pipette) to a beaker, bring

Ferric Oxid and Alumina.

to a boil, add ammonia in slight but distinct excess, boil a few minutes, allow to stand until the precipitate has settled, and filter through a weighed Gooch crucible, taking care not to disturb the precipitate. Dissolve the precipitate in a few cubic centimeters of hot dilute hydrochloric acid, add 25 cc. of hot water, and reprecipitate with ammonia. Filter, wash with hot water, dry, ignite, and weigh. The increased weight multiplied by 2 gives the weight of ferric oxid and alumina.

Ferric Oxid.

Mr. Hargrove determines the iron in the remaining 100 cc. of the filtrate from the silica, by reduction with stannous chlorid and titration with bichromate solution. See "Determination of Ferric Oxid."

Lime.

To the filtrate from the iron and alumina add ammonia until slightly alkaline, heat to boiling and add drop by drop a saturated solution of ammonium oxalate until in slight excess, continue the boiling for a few minutes and then allow to stand about one hour for the precipitate to settle. Filter through a small filter, wash the precipitate with water to which a little ammonia has been added, dry, transfer to a weighed platinum crucible, and ignite, first at a low heat, then in the flame of a blast-lamp for about twenty minutes. Allow the crucible to cool, moisten the contents with a few drops of concentrated sulfuric acid, cover and place the crucible in an inclined position on a triangle over a low flame. Apply heat gently at the top of the crucible, continuing the heating until fumes of sulfuric acid cease, then raise the flame until the crucible is a faint red. Cool and weigh. Multiply this weight by 2 and then by 0.41185 for the lime, CaO, in the cement.

Magnesia. Evaporate the filtrate to about 150 cc., cool, add 5 cc. of ammonia, then drop by drop 20 cc. of sodium ammonium phosphate (saturated solution) with constant stirring using care not to touch the bottom or sides of the vessel with the rod. Set the beaker in a cool place over night, and in the morning filter through a weighed Gooch crucible, wash with dilute ammonia (1 to 3), dry, ignite, cool, and weigh as $Mg_2P_2O_7$. Multiply this weight by 2 and then by 0.36190 for the magnesia, MgO, in the cement.

Rapid Method by Simple Solution in Dilute Hydrochloric Acid

Weigh into a 4 inch casserole 0.5 gram of finely ground dried cement. Add 10 cc. of dilute (1 : 1) hydrochloric acid and, after stirring for a moment, a few drops of concentrated nitric acid. Evaporate to dryness on a hot plate

Silica.

or sand-bath, keeping the dish covered with a watch-glass supported upon a glass triangle. Bake until all odor of hydrochloric acid has disappeared. Cool the casserole slightly and add 20 cc. of dilute hydrochloric acid. Place the watch-glass tightly upon the casserole and stand on the hot plate for a few moments. Add 50 to 75 cc. of hot water. Heat until all soluble salts are dissolved and filter. Wash the residue upon the filter-paper, first three times with hot water, then once with hot dilute hydrochloric acid, and finally well with hot water. Ignite the precipitate (finishing over a blast-lamp) and weigh as SiO_2.

Ferric Oxid and Alumina.

Heat the filtrate from the SiO_2 to boiling and add ammonia in slight but distinct excess. Again bring to the boiling-point and keep boiling for a minute or so. Allow the precipitated oxids of iron and alumina to settle, and filter. Transfer as much of the precipitate as it is possible to do with a wash-bottle from the beaker to the filter. Remove the filtrate from under the funnel, and in its place stand the beaker in which the precipitation was made. Dissolve the precipitate by running hot hydrochloric acid from a wash-bottle around the edge of filter-paper, and wash the paper free from yellow color with water. Reprecipitate the iron and alumina as before by cautious addition of a slight excess of ammonia to the boiling solution. Filter, wash with hot water, ignite and weigh as ferric oxid and alumina.

To the combined filtrate from the two iron and alumina precipitations, which should measure from 300 to 400 cc., add a few drops of ammonia and bring to a boil. Add 25 cc. of a saturated solution of ammonium oxalate with constant stirring, and stir and boil for a few minutes. Allow the precipitate to settle and filter. Wash with hot water, and determine the calcium in the precipitate by titration with standard permanganate as directed on page 40.

Lime.

Cool the filtrate from the calcium oxalate precipitate, and when it feels thoroughly cool to the hand add with constant stirring 20 cc. of a saturated solution of sodium phosphate. Make strongly ammoniacal with *strong* ammonia, so as not to increase the volume unnecessarily, and set aside in the cold for some hours, or better over night. Filter and wash with a mixture of 1 liter ammonia (0.96 sp. gr.), 2 liters water, 150 grams ammonium nitrate, ignite, without drying the filter-paper, over a low flame until the magnesium pyrophosphate is white or light gray in color. Cool and weigh. Multiply the weight by 0.36190 for magnesia, MgO.

Magnesia.

Mr. Andreas Lundteigen, chemist to the Western Portland Cement Co., proceeds thus in the solution and evaporation of the sample. One-half gram of cement is carefully moistened with from 3 to 5 cc. of water in a 3½ inch evaporating dish, and a few drops of nitric acid and about 5 cc. of concentrated hydrochloric acid added. All lumps are carefully crushed with a glass rod, and the solution evaporated. This is hastened by a current of hot air allowed to play on the surface. The air is heated by passing through a platinum coil placed in the flame below the iron plate on which the evaporation is conducted. By this means in from five to seven minutes the solution can be reduced to a thick jelly, when it should be stirred and then heated more carefully until all the hydrochloric acid is expelled.

Modification of the Above Scheme.

Notes

After fusing silica or silicates with sodium carbonate it will be found best to treat the fused mass with hot water until it is thoroughly disintegrated, and then add hydrochloric acid. The addition of the acid first is likely to cause a gelatinous film of silica to surround the mass and so prevent its decomposition.

Instead of supporting the watch-glass upon a glass triangle, in rapid evaporations, it may be held above the dish by three bits of glass, about two inches long, bent at the middle to form a V, and inverted over the sides of the dish.

Some authorities contend that one evaporation, even when the mass is dried for many hours, fails to render all the silica insoluble. They advise moistening the residue from the first evaporation with water and a few drops of hydrochloric acid and again evaporating to dryness. It is essential, however, whether one or two evaporations are made, that all the hydrochloric acid should be expelled, and also that the temperature of baking is not too high.

Silica is hard to wash and retains alkalies tenaciously. It is well for the inexperienced operator, until he finds out how much washing is required, to test with silver nitrate, and continue the operation until the washings cease to react for chlorids.

Silica may be ignited wet, but care must be taken not to dry the precipitate too quickly over the flame, else the steam in escaping will carry with it fine particles of silica. The best plan is not to place the crucible at first directly over the burner, but instead to one side of a low flame. The silica must be ignited over a blast-lamp in order to drive off the last traces of water, which it holds most tenaciously. Ignition over a Bunsen burner, even for some hours, is insufficient for complete dehydration. The blast-lamp will also help to burn off the last trace of the carbon of the filter-paper.

The purity of the silica can easily be tested, and indeed in accurate work, it should always be done. After burning off the carbon, igniting over a blast and accurately weighing, moisten the silica with dilute sulfuric acid and then half fill the crucible with C. P. hydrofluoric acid. Incline the crucible on a tripod over a burner turned low, in such a way that the flame plays under the upper part of the crucible. This causes a rapid evaporation of the solution. When no more fumes come from the crucible move the burner back until it plays upon the bottom of the crucible and raise the flame until the crucible is cherry-red.

Cool and weigh. The loss represents silica, SiO_2, and the residue in the crucible is usually alumina. Its weight may be added to that of the iron and alumina found by precipitation with ammonia, or the residue may be dissolved in concentrated hydrochloric acid and added to the filtrate from the silica, before the addition of ammonia.

Alumina, Al_2O_3, is soluble to some extent in a large excess of ammonia. If, however, the excess is expelled by boiling, the alumina is again precipitated. The presence of ammonium chlorid in the solution greatly aids in the separation of alumina by ammonia. The precipitate of iron and alumina must be filtered off promptly since the alkaline liquid will absorb carbon dioxid from the air, forming calcium carbonate which would be filtered off with the iron and alumina. For the same reason when for any cause the filtrate from the iron and alumina has to stand some days it should be acidified with hydrochloric acid before setting aside. This is necessary when the calcium is to be determined volumetrically, and it saves trouble elsewhere, since the deposit of calcium carbonate forms as a crust on the sides and bottom of the beaker, and is very difficult to remove, without solution and reprecipitation.

Magnesium hydroxid, $Mg(OH)_2$, is not completely soluble in ammonia. The precipitate is, however, readily soluble in ammonia solutions, containing sufficient ammonium chlorid. The precipitation of the magnesia along with the iron and alumina is insured against by the formation of ammonium chlorid, which takes place before the iron and alumina are precipitated, on adding ammonia to the hydrochloric acid solution. If preferable, the operator can be on the safe side by adding half a gram of the salt itself (ammonium chlorid) to the filtrate from the silica before precipitating the iron and alumina.

The precipitate of iron and alumina always contains more or less lime and magnesia, from which long washing fails to free it. Solution and reprecipitation are, therefore, necessary to get around the difficulty. The precipitate is very apt to contain traces of silica also. Some of this comes from the action of the ammonia on the reagent bottle in which it is kept, some from the action of the alkaline liquid in the beaker in which the precipitation is made, and some which failed to be separated by evaporation in the proper place is also carried down here. Since the impurity usually present in the silica is alumina and that in the alumina is silica, the two sources of error tend to balance each other. If desired the weighed precipitate of ferric oxid and alumina can be dissolved by fusion with potassium bisulfate for some hours, the fused mass dissolved in water, the silica filtered off, weighed, and the weight deducted from that of the iron and alumina.

Calcium oxalate is very insoluble and may be washed with hot water. Some chemists prefer to add a little ammonia to the wash-water, but to the author this seems unnecessary. The precipitate should always be formed in a boiling ammoniacal solution, with stirring, and allowed to settle before filtering. Some chemists heat the ammonium oxalate solution also to boiling before adding to the boiling solution containing the calcium. Sufficient ammonium oxalate should always be added to convert all the magnesium present as well as the calcium to oxalate, else the precipitation of the calcium will be incomplete.

The following is given as a quick method of precipitating the lime: Make the liquid alkaline with ammonia and heat it to boiling. Then take away the flame and add gradually two grams of finely powdered, solid, C. P. ammonium oxalate with constant stirring. Replace the burner under the solution and boil for a few minutes. On taking away, the precipitate will settle in a few minutes and may be filtered off as soon as it does.

Calcium oxalate on ignition over a burner to very faint redness changes to calcium carbonate. If the heating is increased and the blast is used calcium oxid is formed. Instead of weighing as the oxid some chemists prefer to weigh as a sulfate. To do this,[1] dry the precipitate perfectly, detach it as far as possible from the filter to a piece of black glazed paper. Burn the filter-paper in a weighed platinum crucible, and when all carbonaceous matter is burned, brush the precipitate into the crucible from the glazed paper. Drop concentrated sulfuric acid on the precipitate till it is well moistened, avoiding an excess, and heat the crucible under a hood cautiously, from a burner held in the hand, until the swelling of the mass subsides and the excess of sulfuric acid has been driven off, as shown by the disappearance of the white fumes coming from the crucible. Then heat for five minutes to a cherry-red heat, but do not use the blast. Cool and weigh as

---

[1] Lord: "Notes on Metallurgical Analysis," p. 11.

calcium sulfate, which multiplied by 0.41185 gives the equivalent of lime, CaO. The third scheme above also gives a method of converting the oxalate to sulfate.

Mr. W. H. Hess, chemist for the Omega Portland Cement Co., uses the following method[1] for converting the calcium oxalate to calcium sulfate. After burning off all the carbon of the filter-paper, the crucible is allowed to cool partly when a portion of chemically pure dry ammonium nitrate, approximately equal in bulk to the lime in the crucible, and about twice as much chemically pure fused ammonium sulfate are added. A tight-fitting cover is now placed on the platinum crucible and then gentle heat is applied. Mr. Hess found it very convenient to incline the crucible at an angle of 30°, allowing the tip of the crucible cover to project outward and then apply the flame to the tip of the cover, gradually bringing the flame under the crucible as the reaction grows less and less violent. The reaction is complete when fumes of ammonia salts are no longer driven off. Intense ignition is unnecessary and is to be avoided. The crucible should be weighed with its cover.

The volumetric method for determining calcium, given a little further on, also gives very accurate results.

If, on evaporation of the filtrate from the lime, a white precipitate settles out, it should be redissolved in a little hydrochloric acid. In concentrating this filtrate it is well to make acid with hydrochloric acid before starting the evaporation.

---

[1] J. Am. Chem. Soc., **22**, 477.

Magnesium pyrophosphate is quite soluble in hot water, less so in cold water, and practically insoluble in water rendered strongly ammoniacal. It should be washed, therefore, with a mixture of water and ammonia. Some chemists use no ammonium nitrate in their washing fluid, and mix in proportions varying from ten to three parts water for one part of ammonia. It is a difficult precipitate to ignite perfectly white, but the blast-lamp should never be used in the attempt to make it so, as destruction of the platinum crucible might follow. The precipitate may be ignited wet if a low flame is used at first.

The Gooch crucible, mentioned in one of the above schemes, consists of a flat-bottomed, perforated crucible provided with a cap (Fig. 2). The perforated crucible is placed in one end of a piece of soft rubber tubing of large bore, the other end of which is stretched over a small funnel passing into a flask through a rubber stopper (Fig. 3). The flask is connected with the filter pump. To prepare the filter, pour a little prepared asbestos (purified by washing with hot concentrated hydrochloric acid) suspended in water into the crucible and attach the suction to the flask. The asbestos at once forms a thick felt over the bottom of the crucible,

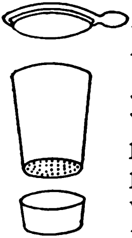
Fig. 2.

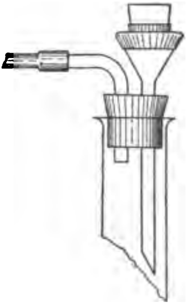
Fig. 3.

which by using the suction may be readily washed with water. After washing, suck dry as possible with the pump, remove from the funnel, detach any pieces of asbestos that may be on the outside of the bottom of the crucible, cap, ignite, and weigh. Remove the cap, attach to the funnel as before, apply the suction and pour the liquid to be filtered through the crucible, wash, cap, dry, if necessary, ignite and weigh as before. The crucible and cap may be purchased from dealers in platinum or chemical ware.

Volumetric Determination of Calcium

Preparation of the Standard Permanganate.

Dissolve 22.56 grams of pure crystallized potassium permanganate in 750 cc. of cold distilled water in a beaker, cover with a watch-glass and allow to stand over night. In the morning filter through asbestos into a large bottle and add 1250 cc. of distilled water. This will give a solution each cubic centimeter of which should be equivalent to about 0.01 gram of lime or 2.0 per cent when a 0.5 gram sample is used. To standardize the solution: Weigh into each of two beakers 1.4 grams of pure crystallized ferrous ammonium sulfate, add cold water, allow the salt to completely dissolve without stirring and then add 10 cc. of dilute sulfuric acid. Stir and run in the permanganate from a burette until the color of the solution in the beaker just changes to pink. The weight of the double salt used divided by 14, and then by the number of cubic centimeters of permanganate required, will give the lime, CaO, value per cubic centimeter for the permanganate. The duplicate titrations should check closely; if not, another pair should be run. For other methods of standardizing the permanganate solution see "Determination of Ferric Oxid."

Determination.

Precipitate the silica and the iron and alumina in the usual way. Heat the filtrate to boiling, add 25 cc. of saturated ammonium oxalate solution, stir well, and after removing the beaker from the source of heat, allow the precipitate to settle. Filter and wash well with hot water. Now punch a hole in the bottom of the filter-paper and wash as much as possible of the precipitate into a large beaker, flask or porcelain dish. Wash the filter-paper with small quantities of hot dilute sulfuric acid from a wash-bottle, and then well with hot water. Dilute the solution to 300 or 400 cc., add 10 cc. of dilute sulfuric acid and warm to 60° or 70° C. When all the precipitate has dissolved titrate the solution with the standard permanganate. Multiply the number of cubic centimeters of permanganate required by the lime value of the standard solution and divide the product by the weight of cement taken for a sample. The result multiplied by 100 will be the per cent of lime, CaO, in the cement.

Notes

The method depends upon the reaction between oxalic acid and potassium permanganate.

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

The reaction between iron and permanganate is

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

Hence 5 molecules $H_2C_2O_4$ = 2 mols. $KMnO_4$ = 10 mols. $FeSO_4$ or 5 mols. $H_2C_2O_4$ (= 5 mols. CaO) = 10 mols. $FeSO_4$ (= 10 atoms Fe).

Then 5 mols. CaO = 10 atoms Fe, and 5(40 + 16) CaO = 10 × 56 Fe, or 280 CaO = 560 Fe.

Hence, CaO : Fe :: 280 : 560, from which CaO = $\frac{280}{560}$ Fe or $\frac{1}{2}$ Fe.

So the iron value of any permanganate solution divided by 2 will give its lime value.

Instead of punching a hole in the filter-paper some operators prefer to dissolve the precipitate in very dilute hydrochloric acid, using as small a quantity as possible; washing the paper thoroughly with hot water and, after adding some sulfuric acid and heating to 60° C., titrating with permanganate. Provided the quantity of hydrochloric acid used for solution is kept small the results will be perfectly accurate and probably time can be saved by proceeding thus.

Volumetric Determination of Magnesium

Dissolve 12.29 grams of pure arsenious acid, As_2O_3, in nitric acid, avoiding a large excess. Evaporate to dryness on a water-bath and neutralize with sodium carbonate after dissolving the residue in a little water. Pour the solution into a graduated liter flask and after rinsing out the dish into this latter dilute to the mark. Each cubic centimeter of this solution is equivalent to 0.005 gram of magnesia, MgO.

Standard Sodium Arsenate.

Dissolve 49.314 grams of pure crystallized sodium thiosulfate in 2000 cc. of water. One cc. of this solution should be equivalent to 0.002 gram of magnesia, MgO. To standardize, measure with a pipette 10 cc. of the standard sodium arsenate solution into a small beaker or dish, add 3 to 5 grams of potassium iodid and 25 cc. of hydrochloric acid (sp. gr. 1.10) and without diluting titrate with the standard thiosulfate until the liquid is colorless. It is not necessary to add starch as an indicator as the end reaction is clear enough without it and the change from pale straw color to colorless is sudden and perfectly distinct. Since 10 cc. of the arsenate solution represents 0.05 gram of magnesia, 0.05 divided by the number of cubic centimeters of thiosulfate required will give the magnesia, MgO, value per cubic centimeter of the standard thiosulfate.

Standard Sodium Thiosulfate.

Separate the silica, iron and alumina, and lime, in the usual manner, taking care, however, to use only a slight excess of ammonium oxalate in precipitating the lime. Place the filtrate from the calcium oxalate in a large Erlenmeyer flask or a gas-bottle of sufficient capacity. Add one-sixth the volume

The Determination.

of the liquid of strong ammonia and 50 cc. of a 10 per cent solution of sodium arsenate. Cork up tightly and shake vigorously for ten minutes. Allow the precipitate to settle somewhat and wash with a mixture of three parts water and one part strong ammonia until the washings cease to react for arsenic. Avoid using an excess of washing fluid, however. Dissolve the precipitate in dilute hydrochloric acid (1 : 1) allowing the acid solution to run into the flask in which the precipitation was made and wash the filter-paper with dilute acid until the washings and solution measure 75 to 100 cc. Cool if not already so and add from 3 to 5 grams of potassium iodid, free from iodate, allow the solution to stand a few minutes and titrate with the standard thiosulfate until the color of the liberated iodin fades first to a pale straw color, and then disappears altogether.

Notes

This method depends upon the fact that magnesium can be entirely precipitated from strongly ammoniacal solution as magnesium ammonium arsenate by addition of sodium arsenate. The arsenic is then determined volumetrically and from this the magnesium calculated.

From the formula of the double salt, $Mg_2(NH_4)_2As_2O_8 + H_2O$, it will be seen that one atom of arsenic, As, is equivalent to one of magnesia, MgO, and consequently the ratio of magnesia to arsenious acid, As_2O_3, is $2(24.28 + 16) : (75.01 \times 2 + 16 \times 3)$ or $80.56 : 198.02$, from which $MgO = 0.4068 \times As_2O_3$.

When a solution of arsenic acid contains sufficient sulfuric or hydrochloric acid, the arsenic is quickly reduced from the higher to the lower state of oxidation even in the cold, according to the reaction

$$As_2O_5 + 4KI + 4HCl = As_2O_3 + 5KCl + 2H_2O + 2I_2.$$

The liberated iodin is titrated with thiosulfate when the following reaction takes place:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

On adding the potassium iodid to the acid solution a brown precipitate forms which, however, disappears when the thiosulfate is added. The complete reduction of the arsenic only takes place in very acid solutions, hence the precipitate of magnesium ammonium arsenate should be dissolved in and the filter-paper washed with dilute hydrochloric acid (1 : 1). The precipitate of magnesium ammonium arsenate is less soluble when an excess of sodium arsenate is present in the ammoniacal solution. It is more soluble when a large excess of ammonium oxalate has been used to precipitate the lime; consequently guard against adding much more ammonium oxalate than is necessary to entirely precipitate the lime and add a considerable excess of sodium arsenate in precipitating the magnesia. The precipitate must be washed with dilute ammonia as it is soluble in water and, as it is not entirely insoluble in ammonia, the volume of the washing fluid should be kept as small as possible.

Agitation greatly hastens the precipitation of the magnesia. An ordinary "milk shake" apparatus will be found

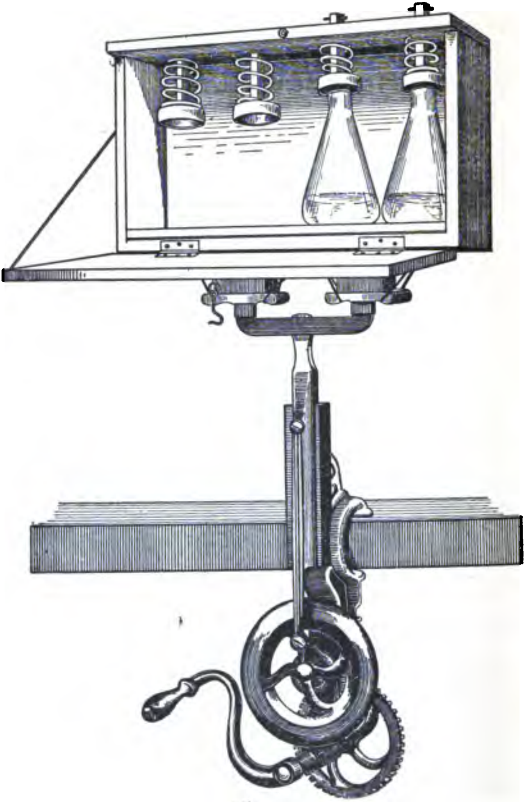

Fig. 4.

very convenient for shaking, if provided with an arrangement for holding the flasks (see Fig. 4). The precipitate is very heavy and settles rapidly.

Instead of standardizing the solution against a standard solution of sodium arsenate, bichromate or permanganate, whose iron value is known, may be used. Measure into a beaker from a burette such a quantity of standard bichromate or permanganate as is equivalent to 0.1389 gram of metallic iron, add a little dilute sulfuric acid and 1 gram of potassium iodid and titrate with the standard thiosulfate until the yellow color almost fades, then add a little boiled starch solution and titrate until the blue color of the starch entirely disappears. 0.1389 gram of metallic iron is equivalent to 0.05 gram of magnesia. To find the magnesia value, therefore, of the thiosulfate divide 0.05 by the number of cubic centimeters of thiosulfate required. The calculation is explained as follows:

(I). $K_2Cr_2O_7 + 6KI + 14HCl = 8KCl + Cr_2Cl_6 + 7H_2O + 6I$

(II). $K_2Cr_2O_7 + 6FeCl + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + 3Fe_2Cl_6$.

(III). $As_2O_5 + 4KI + 4HCl = As_2O_3 + 4KCl + 2H_2O + 4I$.

From (I) and (II) 6 atoms I = 1 mol. $K_2Cr_2O_7$ = 6 atoms Fe.
From (III) 2 atoms As = 4 atoms I.

1 atom As = 1 mol. MgO = 2 atoms I.
3 mols. MgO = 6 atoms I = 6 atoms Fe.

$3(24.3 + 16)$ MgO = 120.9 MgO = 6×56 Fe = 336 Fe.
$120.9 : 336 :: 0.05 : x \qquad x = 0.1389$.

Rapid Determination of Silica and Lime in Cement

It is frequently desirable to know the percentage of silica and lime present in a cement without regard to the ferric oxid and alumina and the magnesia. The following rapid method, communicated to the author by Mr. Andreas Lundteigen, chemist of the Western Portland Cement Co., Yankton, S. D., is designed to meet this end.

Carefully moisten 0.5 gram of cement with from 3 to 5 cc. of water in a 3½ inch evaporating dish or casserole. Add 5 cc. of concentrated hydrochloric acid and a few drops of nitric acid and carefully crush all lumps with a glass rod. Evaporate the solution quickly on a hot plate by allowing a current of hot air to play upon its surface (see page 32). In from five to seven minutes the contents of the dish will have become a stiff jelly. Stir this in order to make the silica granular and easier to filter, and heat the dish more carefully until all the hydrochloric acid is expelled. Redissolve the residue in hydrochloric acid and water, filter, ignite and weigh the silica, SiO_2, as usual.

Dilute the filtrate to 250 cc., bring to a boil and add enough ammonia to precipitate all the iron and alumina. Again bring to a boil, and while in this condition, add oxalic acid solution, drop by drop, until the red color of the iron has disappeared, then precipitate the lime by adding an excess of ammonium oxalate. Allow to settle, filter, wash and determine by titration with standard potassium permanganate as described on page 40.

Determination of Ferric Oxid

By Titration with Potassium Bichromate

(Penny's Method)

Standard Potassium Bichromate.

Place from 10 to 15 grams of C. P. potassium bichromate in a sufficiently large platinum crucible. Heat carefully, avoiding all contact of the flame with the contents of the crucible, until the salt just fuses to a dark liquid. Then withdraw at once from the flame and let the crucible cool. Weigh 3.074 grams of the fused bichromate, which in cooling will have crumbled to a powder, dissolve in 250 to 300 cc. of cold water and pour into a liter graduated flask. Rinse out the beaker several times into the flask and dilute the solution to the liter mark. Mix well. One cc. of this solution should be equivalent to 0.005 gram of ferric oxid, Fe_2O_3.

To test or standardize the solution, weigh into a small beaker 0.4900 gram of pure ferrous ammonium sulfate (equivalent to 0.1 gram of ferric oxid). Dissolve in 50 cc. of water and, when all the salt is in solution, add 5 cc. of dilute hydrochloric acid. Run the bichromate solution from a burette into the liquid in the beaker until a drop of the iron solution placed upon a white porcelain plate and mixed by stirring with a drop of a freshly made 1 per cent solution of potassium ferricyanid no longer assumes a blue color, but instead gives a yellow. This should require 20 cc. of the bichromate solution. If more or less, repeat the test, and if the first and second results agree, divide 0.1, the ferric oxid equivalent of the weight of the ferrous ammonium sulfate used, by the number of cubic centimeters of bichromate required. The result will give the ferric oxid equivalent, or value, in grams for each cubic centimeter of the standard potassium bichromate.

Some operators prefer to standardize their bichromate against iron wire. In this case clean 0.1 gram of fine iron wire by rubbing between fine emery paper and then between filter-paper. Coil around a lead pencil and weigh. Drop the coil in a small beaker, add 20 cc. of dilute hydrochloric acid and heat until all the wire dissolves. Wash down the sides of the beaker with a wash-bottle, bring the contents to a boil and drop in the stannous chlorid solution, described below, slowly until the last drop turns the solution colorless. Remove from the source of heat and cool the liquid rapidly by setting the dish in a vessel of cold water. When nearly cold add at once 15 cc. of saturated mercuric chlorid solution, and stir well. Allow to stand a few minutes and titrate with the bichromate as described above. Multiply the weight of the iron wire by 0.003 and deduct this from the original weight, for impurities in the wire. The corrected weight divided by 0.7 and then by the number of cubic centimeters of bichromate required, gives the ferric oxid equivalent in grams to each cubic centimeter of the standard bichromate. This value should be checked unless within the limits of allowable error to 0.005 gram.

Stannous Chlorid Solution.

Dissolve 100 grams of stannous chlorid solution in a mixture of 300 cc. of water and 100 cc. of hydrochloric acid. Add scraps of metallic tin and boil until the solution is clear and colorless. Keep this solution in a closely stoppered bottle (best a dropping bottle) containing metallic tin. This solution should be kept from the air.

$MgCl_2$ Sol.

Make a saturated solution of mercuric chlorid by putting an excess of the salt in a bottle and filling up with water and shaking as the solution gets low.

The Determination.

Weigh 1 gram of finely ground cement into a small beaker and add 15 cc. of dilute hydrochloric acid, heat from ten to fifteen minutes and add a little water. Heat to boiling and filter through a small filter, washing the residue well with water and catching the filtrate and washings in a porcelain dish. Add to the solution 5 cc. of dilute hydrochloric acid and bring to a boil. Add carefully, drop by drop, the stannous chlorid solution until the last drop makes the solution colorless. Remove from the burner and cool the liquid by setting in a vessel of cold water. When nearly cold add 15 cc. of the mercuric chlorid solution and stir the liquid in the dish with a glass rod. Allow the mixture to stand for a few minutes, during which time a slight white precipitate should form. Run in the standard bichromate solution carefully from a burette until a drop of the iron solution tested with a drop of 1 per cent solution of potassium ferricyanid no longer shows a blue, but instead a yellow color. Multiply the number of cubic centimeters of bichromate used by the ferric oxid equivalent per cubic centimeter of the bichromate and divide the product by the weight of the sample. The result multiplied by 100 gives the per cent of the ferric oxid, Fe_2O_3, in the cement.

Notes

Treatment with hydrochloric acid is sufficient to dissolve all except a mere trace of iron in Portland cement.

A strongly acid solution of ferric chlorid, if boiling hot, is instantly reduced to ferrous chlorid by a solution of stannous chlorid according to the following reaction:

$$Fe_2Cl_6 + SnCl_2 = SnCl_4 + 2FeCl_2.$$

The operator can tell when complete reduction has taken place by the disappearance of the yellow color of the solution. The excess of stannous chlorid is removed by addition of mercuric chlorid when the following takes place:

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2.$$

The precipitate, Hg_2Cl_2, should be white; if colored gray too much stannous chlorid was used in reduction and mercury has been formed. As mercury reacts with the bichromate, when the precipitate formed on adding mercuric chlorid is not perfectly white, but is colored gray, the determination should be repeated, using more care to avoid a large excess of the tin solution. If no precipitate is formed on addition of mercuric chlorid, the stannous chlorid has not been added in excess, and all the iron will not have been reduced to the ferrous state.

Ferrous salts are oxidized to ferric compounds by bichromate when in a solution containing a considerable excess of hydrochloric or sulfuric acid. The reaction is:

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 3Fe_2Cl_6 + Cr_2Cl_6 + 2KCl + 7H_2O$$

The ferrous ammonium sulfate has the formula $Fe(NH_4)_2(SO_4)_2.6H_2O$. It, therefore, contains one-seventh its weight of iron and is equivalent to 0.20408 of its weight of ferric oxid, Fe_2O_3.

To make a 1 per cent solution of potassium ferricyanid, dissolve 1 gram of the salt in 100 cc. of water. Ferric compounds give a yellow color to this solution, while ferrous compounds impart an intense blue color. This solution must always be made up fresh as it is reduced by exposure to light.

By Titration with Potassium Permanganate

(Marguerite's Method)

Dissolve 1.975 grams of pure crystallized potassium permanganate in a liter of water, allow to stand all night and in the morning filter through asbestos into a bottle. To test, or standardize, the solution, weigh into each of two beakers 0.4900 gram of pure ferrous ammonium sulfate, equivalent to 0.1 gram of ferric oxid, Fe_2O_3. Dissolve in 50 cc. of water, without heating, add 10 cc. of dilute sulfuric acid and run in the permanganate from a burette un-

Standard Potassium Permanganate.

til the color of the solution in the beaker just begins to turn pinkish. Take the reading of the burette and then add another drop, which should cause the solution to become decidedly pinkish. Divide the weight of ferric oxid (0.1 gram) equivalent to the weight of ferrous ammonium sulfate taken for the titration (0.49 gram) by the number of cubic centimeters of permanganate required; the result will give the ferric oxid equivalent to 1 cc. of the permanganate.

To use iron wire in standardizing, clean two pieces of fine iron wire, weighing 0.1 gram each, by rubbing first between emery paper and then with a cloth. Coil around a lead pencil and weigh each coil. Put 30 cc. of dilute sulfuric acid in a strong gas bottle provided with a perforated stopper through which passes a perfect fitting glass tube with a hole blown in its side (Fig. 5). Heat the acid to boiling and drop in a coil of wire. When the solution of the latter is complete, remove the bottle from the source of heat and, after closing the opening by pushing the perforated glass tube down until its opening is closed by the stopper, allow the gas-bottle to cool. When cold titrate the solution with the permanganate solution as above. Multiply the weight of the iron wire by 0.003 and deduct the result from the original weight for impurities. Multiply the corrected weight by 1.4286, or divide by 0.7, and divide by the number of cubic centimeters of permanganate

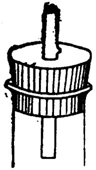

Fig. 5.

required. The result will be the ferric oxid equivalent of 1 cc. of the standard potassium permanganate. Repeat the test with the other weighed coil of iron wire. The values for each cubic centimeter of permanganate by the two titrations should agree closely. Yet another way is to dissolve the iron wire in 15 cc. of dilute sulfuric acid in a beaker, cool, dilute, pass through the reductor, and titrate with the permanganate, calculating the results as above.

The following "simplified reductor" is the design of Dr. Porter W. Shimer, of Lafayette College. His description of the apparatus[1] is as follows: "The reductor tube (Fig. 6) is a plain glass tube, three-eighths inch internal diameter, drawn out and cut off at its lower end. It is filled by placing a few small pieces of broken glass in the drawn-out portion, and on this about an inch of well cleaned sand. The tube is then filled with amalgamated zinc of as nearly uniform twenty mesh size as possible. About 80 grams are required. No asbestos or glass wool is used. The sand prevents particles of zinc from falling through and it does not become clogged by use. * * * The consumption of zinc is very small, and when the column

Apparatus.

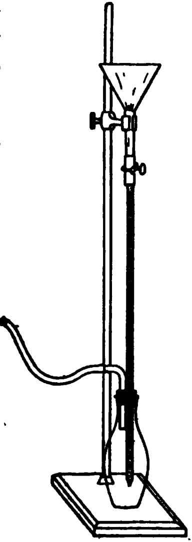

Fig. 6.

---

[1] J. Am. Chem. Soc., 21, 723.

has settled about an inch a little fresh zinc can easily be poured in from above. The reductor tube is united with a 4 inch funnel by means of rubber tubing, well tightened with wire. Between the funnel and reductor is a Hoffman clamp. The lower end of the tube passes through a soft two-hole stopper so far as to reach half way to the bottom of a heavy-walled pint gas-bottle. The gas-bottle is connected with a filter-pump through an intermediate safety bottle and valve. The funnel is clamped to a retort stand in such a manner as to allow the tube and gas-bottle to swing easily in all directions. It is well to adjust the height so as to leave the gas-bottle raised slightly above the base. The passage of the suction through the reductor may be effected either by use of the pump or by means of the vacuum obtained by condensation of steam, devised originally in Bunsen's laboratory. In using the latter method a little water may be boiled in the gas-bottle until all air is expelled, and then quickly unite with the reductor, the clamp on the filter-pump being closed. The speed of filtration is regulated by the upper clamp. Instead of filling the gas-bottle with steam by boiling water in it, it is better to have a convenient tin or copper can containing boiling water and provided with one or more short steam outlet tubes on top. The empty gas-bottle is inverted over one of these steam outlets and, when filled with live steam, is taken off and united as quickly as possible with the reductor. This latter method has the advantage of starting with an empty gas-bottle which is desirable on the score of accuracy both in iron and phosphorus determinations."

To use the reductor first pass, by the aid of suction, about 50 cc. of cold dilute sulfuric acid (1 part acid to 20 parts of water) through the reductor, and then follow with 200 cc. of cold distilled water. The Hoffman clamp should be closed before all the water has run out of the funnel so as to keep the tube full of water. Now empty the flask, again attach to the tube, pour the iron solution into the funnel and open the clamp. Just before the funnel becomes empty, run water around its sides and rinse the beaker well with water, running the washings also through the reductor, using about 100 to 150 cc. of water to wash the funnel and beaker. The time required for the iron solution to filter through the zinc, should be regulated by the upper clamp to occupy from three and a half to five minutes.

Determination.

Weigh 1 gram of finely ground cement into a beaker and add 15 cc. of hydrochloric acid. Heat for ten to fifteen minutes, add 200 cc. of water and heat to boiling. Add ammonia in slight but distinct excess, boil a few minutes, allow the precipitate to settle, filter, using the filter-pump if one is at hand, and wash two or three times with hot water. Place a clean flask under the funnel and redissolve the precipitate in a mixture of 15 cc. dilute sulfuric acid, 60 cc. water, made up in the beaker in which the precipitation was effected. Wash the filter and silica free from iron with cold water, pass through the reductor and titrate the solution with permanganate. Multiply the number of cubic centimeters of standard permangaante required by the ferric oxid value of the permanganate and then by 100. Divide the result by the weight of cement taken; the quotient will be the per cent of ferric oxid, Fe_2O_3, in the cement.

Notes

Ferrous salts are oxidized by potassium permanganate in solutions containing free acid to ferric salts according to the reaction,

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Potassium permanganate does not give trustworthy results in the presence of free hydrochloric acid. Owing to its liability to be changed by light and with time, it should be kept in the dark and restandardized every few months.

Instead of reducing the iron solution by means of a reductor, the gas-bottle, mentioned on page 54, may be used. Pour the solution into the bottle. Add 1 gram of granulated zinc, stopper and allow to stand until the evolution of hydrogen slackens; then heat to boiling. When the zinc is completely dissolved (it may be necessary to add more acid to effect this), push down the glass tube, cool, and after adding 10 cc. of dilute sulfuric acid titrate with the permanganate.

If desired the residue left on dissolving the ferric oxid and alumina in sulfuric acid may be ignited to destroy the filter-paper, moistened with dilute sulfuric acid, and then dissolved in hydrofluoric acid. This latter may then be gotten rid of by evaporation until sulfuric acid fumes begin to come from the crucible. The residual liquid is to be washed into the solution of the ferric oxid and alumina, and the whole, after reduction, titrated with standard permanganate.

If the iron were determined in cement as in iron ores by dissolving in dilute hydrochloric acid and evaporating with sulfuric acid until the former has been expelled, calcium sulfate would be formed. This would fail to entirely dissolve on diluting with water and would, on attempting to free the iron solution from the insoluble matter, clog up the filter-paper making a tedious filtration. The method given is much more satisfactory and saves time.

Determination of Sulfuric Acid

By Solution in HCl

Weigh 1 gram of finely ground dried cement into a casserole or dish and add 15 cc. of dilute hydrochloric acid and 5 cc. of concentrated nitric acid. Evaporate the solution to dryness and heat until all odor of hydrochloric acid has disappeared from the contents of the dish. Cool, add 5 cc. of hydrochloric acid and heat for a few moments, then add 50 cc. of hot water, digest a little while and filter off the silica. Heat the filtrate from the silica to boiling and add 10 cc. of boiling 10 per cent barium chlorid solution. Stir well and allow to stand over night. Filter, ignite, and weigh as $BaSO_4$, which multiplied by 0.34291 gives SO_3, or by 0.58565, gives calcium sulfate, $CaSO_4$. In this latter case multiply the percentage of calcium sulfate by 0.41185 and deduct from the percentage of lime for the true percentage of calcium oxid, CaO.

By Fusion with Na_2CO_3 and KNO_3

Place 1 gram of cement, finely ground and dried, in a large platinum crucible and thoroughly mix it by stirring with 6 grams of sodium carbonate and a little sodium or potassium nitrate. Heat the mixture, gently at first, over a Bunsen burner for a while and then over a blast-lamp until the contents of the crucible are in quiet fusion. Run the fused mass well up on the sides of the crucible and chill by dipping the bottom of the crucible in a vessel of cold water. If loose, remove the mass from the crucible to a casserole or dish, and cover with hot water. If not loose, fill the crucible with hot water and digest until the mass breaks up ; then remove to the dish. Cover the latter with a watch-glass and add 20 cc. of dilute hydrochloric acid. When effervescence ceases remove the watch-glass, rinse into the dish and evaporate the solution to complete dryness. Place the dish in an air-bath and heat at 110° C. for one hour. Cool the casserole somewhat and add 5 cc. of dilute hydrochloric acid and 50 cc. of hot water. Heat until the solution boils, filter and wash. Heat the filtrate to boiling and add, drop by drop, with stirring 10 cc. of a 10 per cent solution of barium chlorid, also brought to boiling. Continue the boiling and stirring for a few minutes, remove the beaker to a warm place and allow to stand over night. Decant the clear solution, without disturbing the precipitate, through a 9 cm. filter-paper, wash the precipitate once or twice with hot water by decantation, then transfer it to the filter-paper and wash well with hot water. Dry, ignite, and weigh as barium sulfate, $BaSO_4$. Multiply this weight by 0.34291 for SO_3.

Notes

When rapid sulfuric acid determinations are desired the precipitate of barium sulfate may be filtered off in one hour after precipitation, or as soon as it has settled. Newberry states that the error will not exceed 3 per cent of the total sulfuric acid present, by this shortening of the time allowed for precipitation.

Some chemists prefer to work with a larger sample than 1 gram when determining sulfuric acid by solution. Indeed when the cement is very low this may be necessary. From 3 to 5 grams can be taken for a sample, provided the quantity of acid used to decompose the cement and that of barium chlorid to precipitate the sulfur, are increased also.

A weighed Gooch crucible[1] with its asbestos felt filter may conveniently be substituted for the filter-paper to collect the barium sulfate precipitate.

Determination of Sulfur Present as Calcium Sulfid

Weigh 5 grams of cement into a porcelain dish, and triturate with water until it shows no further tendency to set. Then wash out into the flask (Fig. 7) and cork tightly. Two-thirds fill the ten-inch test-tube with a solution of

---

[1] See page 39.

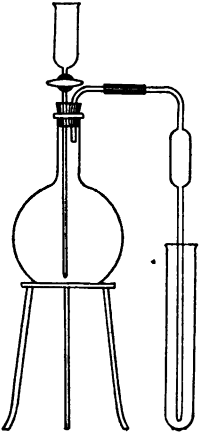

Fig. 7.

lead oxid in caustic potash made by adding lead nitrate solution to potassium hydroxid solution (sp. gr. 1.27) until a permanent precipitate forms, and then filtering off the solution through asbestos after allowing the precipitate to settle. Run into the flask by means of the funnel 50 cc. of dilute hydrochloric acid and apply heat gently. Finally bring the acid to a boil and disconnect the delivery tube from the flask at the rubber joint. Collect the precipitate on a small filter, wash it once with water and then while still moist throw the precipitate and filter back into the test-tube, in which has been placed some powdered potassium chlorate. Pour upon the filter and precipitate 10 cc. of concentrated hydrochloric acid. Allow to stand in a cool place until the fumes have passed off, then add 25 cc. of hot water, filter off the pulp, etc., and wash with hot water. Heat the filtrate to boiling and add ammonia until the solution is slightly alkaline. Then acidulate with a few drops of hydrochloric acid, add 10 cc. of a 10 per cent solution of barium chlorid, also brought to a boil, boil for a few minutes and stand in a cool place over night. Filter, wash, ignite, and weigh as barium sulfate. Multiply this weight by 0.30895 for calcium sulfid, CaS, or by 0.13734 for sulfur, S.

Notes

Instead of alkaline lead nitrate solution, a solution of cadmium chlorid made slightly alkaline with ammonia may be used to absorb the evolved hydrogen sulfid, in which case the cadmium sulfid precipitated, may be collected upon a previously weighed filter-paper, dried, weighed and the sulfur calculated from this weight. For this method use 10 grams of cement for the sample and fill the test-tube two-thirds full of a solution of cadmium chlorid, made by dissolving 3 grams of cadmium chlorid in 75 cc. of water, adding ammonia until the precipitate at first formed redissolves and then diluting to 500 cc. Proceed as usual. Collect the precipitate of cadmium sulfid upon a small counterpoised filter, or better in a Gooch crucible and felt, wash with water to which a little ammonia has been added, dry at 100° C. and weigh as cadmium sulfid, CdS. The weight of cadmium sulfid multiplied by 0.5000 gives the equivalent amount of calcium sulfid. Calculate the percentage and report as such. Calculate the total sulfur, as found by either of the methods on pages 59–60 to calcium sulfate, by multiplying the weight of the barium sulfate by 0.58565. Now multiply the percentage of calcium sulfate so found by 0.41185 and deduct the product from the percentage of lime (as found by precipitation as oxalate in the general scheme). The difference should be reported as calcium oxid or lime, CaO.

Multiply the percentage of calcium sulfid by 1.8872 for its equivalent in calcium sulfate and deduct from the percentage of total sulfur calculated as calcium sulfate. Report the difference as calcium sulfate.

Determination of Carbon Dioxid and Combined Water

Cements contain carbon dioxid, the amount varying from a mere trace in a fresh well burned Portland cement to a large percentage in natural cements. Combined water is also present in cements; the amount is, however, usually very small.

Apparatus.

For carrying out the determination of carbon dioxid and combined water at the same time, the apparatus designed by Dr. Porter W. Shimer, of Lafayette College, Easton, Pa., for carbon combustions,[1] is best suited.

The apparatus as used for carbon dioxid and combined water determinations is illustrated in Fig. 8. It consists of the following parts:

1. Two aspirator bottles, *a′* and *a″*, the upper, *a′*, filled with distilled water and the tube leading to the lower bottle extending to the bottom of the latter.

2. A potash bulb, *b*, containing a solution of caustic potash of 1.27 sp. gr. The form of bulb shown in the cut is Liebig's. Mohr's or any other form will do as well, but the Liebig bulb is the cheapest and answers as well here as the more expensive forms.

---

[1] J. Am. Chem. Soc., 21, 557.

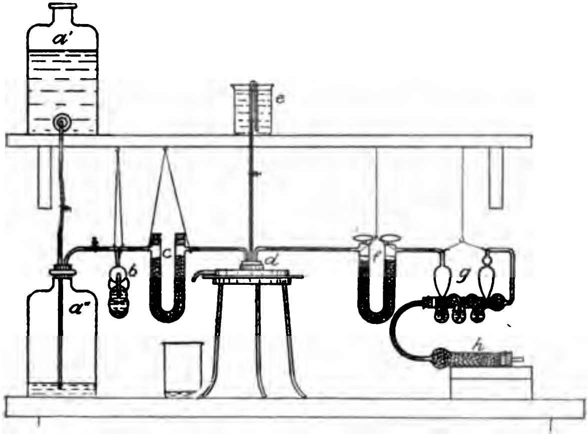

Fig. 8.

3. A **U** tube, *c*, filled with dried granular calcium chlorid. A straight calcium chlorid tube may be used in place of the **U** tube. It takes up more room, however.

4. A platinum crucible, *d*, provided with a water-cooled stopper and reservoir, *e*, for supplying water to this latter, and a round water trough resting upon asbestos board upon a tripod. Fig. 9 shows the crucible stopper, etc., in detail. The dimensions of the crucible should be $1\frac{7}{16}$ inches in diameter and $1\frac{9}{16}$ inches high. The top of the crucible is stiffened by a brazed ring of ordinary sheet copper $\frac{3}{16}$ inch wide, and fitting closely around the extreme top of the crucible. The ring should be made of sheet metal, so as to give the crucible the necessary support against

stretching without making it too rigid. The water-cooled stopper is made of sheet copper, the joints being brazed. The stopper should be made as nearly perfectly circular as is possible, and free from indentations or imperfections in the brazing. The sides of the stopper should not flare more than the sides of the crucible at the top. Too much flare has the tendency to cause the stopper to be forced out when under pressure. The stopper is somewhat smaller in diameter than the crucible opening, in order to allow space for a rubber band. This band may be obtained of stationers, and is of black rubber ¼ to ½ inch wide, and of sufficient length to stretch tightly around the lower part of the stopper. The crucible rests with its bottom through a circular opening in a piece of $\frac{3}{16}$ inch asbestos board which in turn rests upon a tripod. Fig. 9 shows the position of the circular water trough, and Fig. 8 that of the reservoir for supplying water to the stopper.

5. A small U tube, *f*, filled with dried granular calcium chlorid. The best form is that shown, provided with side arms and glass stop-cocks.

6. A potash bulb, *g*, with calcium chlorid tube attached. The bulb should be filled with caustic potash of 1.27 specific gravity, and the tube with dried granular calcium chlorid.

7. A guard tube, *h*, filled with dried granular calcium chlorid.

Fill the reservoir, *e*, with boiling water. Half fill the crucible with freshly ignited asbestos, and close it with the water-cooled stopper. In putting in this latter do not brace the thumb against the overflow tube, as this would risk bending the stopper at the base of the overflow. See that the apparatus is perfectly tight by running the aspirator and pinching the tube together just after the potash bulb.

Testing the Apparatus.

Saturate a long piece of wick with alcohol and wrap it twice around the crucible as the latter rests in its place upon the asbestos board and allow the ends of the wick to lie in the trough as shown in Fig. 9. Open the clamp and allow water to run out of the stopper. Place a Bunsen burner under the crucible. Open the clamp between the lower aspirator bottle and the potash bulb, *b*, and regulate the current of air through the apparatus slowly for about twenty minutes. Detach the potash bulb, *g*, and the calcium chlorid tube, *f*, and weigh. Again connect the bulb and tube in the train

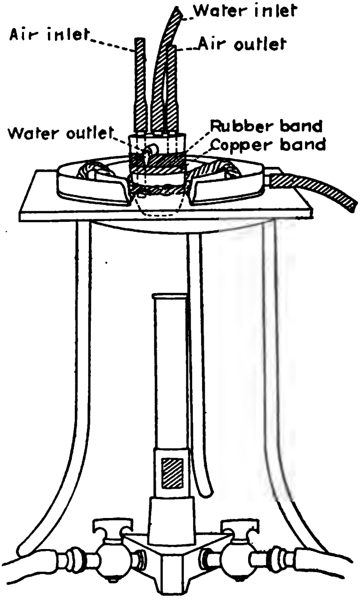

Fig. 9.

and aspirate air slowly through the apparatus for another twenty minutes. Detach the bulb, *g*, and tube, *f*, and again weigh them. This weight should agree to within 0.0005 of the former weight for the potash bulb, and 0.0003 for the calcium chlorid tube. If not, after making sure there is no leakage in the apparatus, repeat the test. When the weights agree within the limits given, take the last pair as the weights of the bulb and tube, and proceed with the determination.

Weigh into the crucible from 2 to 5 grams of cement, cover with ignited asbestos and stopper tightly. Test the apparatus and be sure there is no leakage. Place the Bunsen burner under the crucible after starting the hot water to flowing through the stopper and wrapping the wick around the crucible twice. Cause a slow current of air from the aspirator bottles to flow through the apparatus. After ten minutes replace the Bunsen burner by a blast-lamp and continue the ignition for twenty minutes. Remove the lamp and aspirate air through the apparatus for ten minutes longer. Detach the potash bulb, *g*, and the calcium chlorid tube, *f*, and weigh. The increase in weight of the former represents the carbon dioxid, CO_2, and of the latter water, H_2O.

The Determination.

Notes

In this method the combined water and the carbon dioxid are driven out of the cement by ignition; the former is absorbed in a weighed calcium chlorid tube and the latter in a weighed potash bulb. The increase in weight of the tube and bulb respectively represent the weight of combined water and carbon dioxid in the cement sample. The air entering the apparatus for the purpose of aspiration is purified of any water and carbon dioxid it is sure to contain by passing through caustic potash and then over calcium chlorid.

To make the upper aspirator bottle, bore a hole near the bottom of a five pint bottle with a file dipped in turpentine, and then slip into this hole a bit of glass tube covered with an inch or so of soft, thick-walled rubber tubing.

To fill the potash bulbs attach a short piece of rubber tubing to one end and dipping the other end in the caustic potash solution contained in a shallow dish apply suction to the rubber tubing with the mouth. When the bulbs are filled to the proper height (see Fig. 14) wipe the end dry inside and outside with pieces of filter-paper.

Instead of the bulb, *b*, the air may be purified of any carbon dioxid it contains by causing it to bubble through caustic potash solution contained in two 4 ounce wide-mouthed bottles.

Calcium chlorid sometimes, though not often, contains calcium oxid, which would absorb carbon dioxid. To saturate this, connect the apparatus, leaving out the potash bulb, *f*, and place a small piece of marble in the crucible. Now heat the crucible with a blast-lamp and aspirate air slowly through the apparatus. Then take the marble out of the crucible and aspirate air for twenty minutes longer.

The potash bulbs and U tube should be weighed as follows: Place the bulb upon one balance pan, and on the other the approximate weight. Stand the U tube in the balance case. Close the door and do not open it for exactly twelve minutes. Then finish weighing the bulb so that the exact result is obtained in fifteen minutes from the time the bulb was placed on the pan. Now remove the bulb and weigh the U tube quickly.

When not attached in the train the U tube should have its stop-cocks turned so as to close the openings, and the potash bulb should be "capped" with short pieces of rubber tubing containing, in one end, bits of capillary glass tubing.

It is preferable to weigh the sample into a small basket folded from platinum foil and place this in the ignition crucible rather than weigh the cement into the crucible directly.

If the cement should contain any appreciable quantity of carbonaceous matter, such as unburned coke, this would be burned to carbon dioxid causing high results. In this case first determine the carbon dioxid given off on ignition. Then weigh another sample into the crucible, add a little hydrochloric acid, evaporate to dryness and dry at 100° C., and determine the carbon dioxid in the residue as before. This will represent the carbon dioxid due to the burning of the organic matter. The difference, of course, represents the carbon dioxid present in the cement as carbonate.

A **U** tube, containing soda-lime, may replace the potash bulb, *g*. This tube should be similar to *f*, and provided with ground-glass stoppers. About an inch of calcium chlorid should top the soda-lime in the limb next the guard tube, *h*.

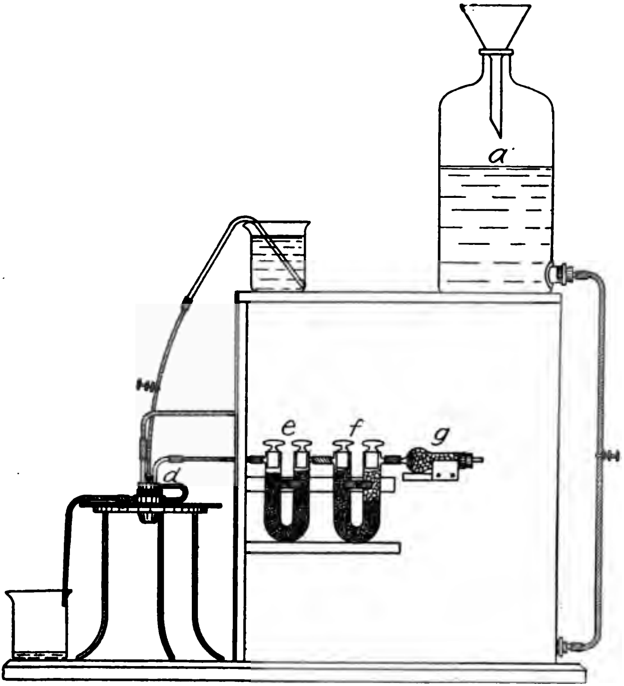

Fig. 10.

When many carbon dioxid determinations have to be made, it will be found convenient to arrange the apparatus on a stand as shown in Figs. 10 and 11. Fig. 10 shows the front of the apparatus and Fig. 11 the reverse. The stand consists of a wooden base 1–1 ½ inches thick, and upon

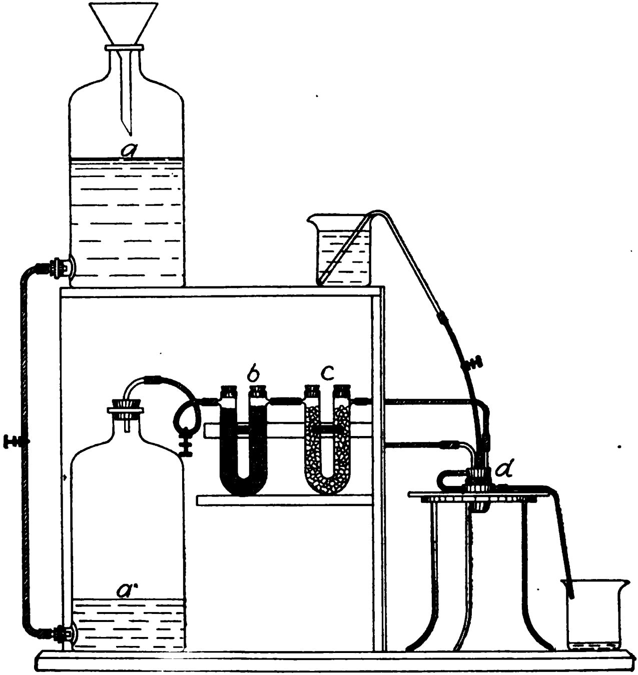

Fig. 11.

this is mounted an upright board. At the end of this board and running entirely across the base is fastened another upright at right angles to the first. These uprights support a shelf upon which rests the upper aspirator bottle and the reservoir for the water-cooled stopper. The upright nearest the tripod should be protected against the heat of the blast-lamp by covering with a sheet of asbestos.

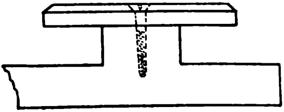

Fig. 12.

The **U** tubes, etc., rest upon shelves as shown. The manner of clamping the **U** tubes to the board is also shown in Fig. 12. *a′* and *a″* (Fig. 11) are aspirator bottles; *b* is filled with soda-lime and *c* with calcium chlorid; *d* is Shimer's special form of water-jacketed platinum crucible; *e* (Fig. 10) is filled with calcium chlorid, *f* with soda-lime topped with calcium chlorid, and *g* with calcium chlorid.

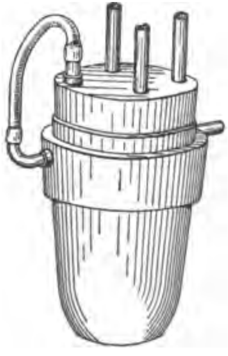

Fig. 13.

Fig. 13 shows Shimer's special form of "water-jacketed crucible." It is more compact than the form shown in Fig. 9 and more easily handled, but is also more expensive.

Determination of Carbon Dioxid Alone

The apparatus just described for carbon dioxid and combined water determinations may, of course, be used for determining carbon dioxid only. In this case it is not necessary to weigh the calcium chlorid tube, *f*, and in place of the expensive **U** tube with its ground-glass stop-cocks, a simple straight form calcium chlorid tube can be used just as well. Neither is it necessary to supply the stopper with hot water, and an empty potash bulb can replace the calcium chlorid tube, *c*. The determination is carried out precisely as if both the water and carbon dioxid were being considered, with, of course, the exception of not weighing the tube, *f*, at the end of the operation. If the stopper is wet with the finger before insertion into the crucible, it will be found to go in easier. This is, of course, not permissible when the water also is determined.

Some chemists prefer to determine carbon dioxid by liberating this constituent with hydrochloric acid and absorbing the evolved gas in a weighed potash bulb.

For carrying out the determination, refer to the apparatus (Fig. 8) for determining carbon dioxid and combined water. Omit the **U** tube, *c*, and substitute for the crucible, *d*, a 100 cc. wide-mouthed flask provided with a funnel tube. Follow the flask with a **U** tube containing sulfuric acid (sp. gr. 1.84) and this by the **U** tube, *f*, the potash bulb, *g*, and the guard tube, *h*.

A convenient way of arranging the apparatus is shown in Fig. 14. *a* is filled with soda-lime; *b* is a funnel tube with ground-glass stop-cock, *c* the 100 cc. flask, *d* contains sulfuric acid, *e* and *g* calcium chlorid, *f* is the weighed potash bulb, and *h* the aspirator bottle.

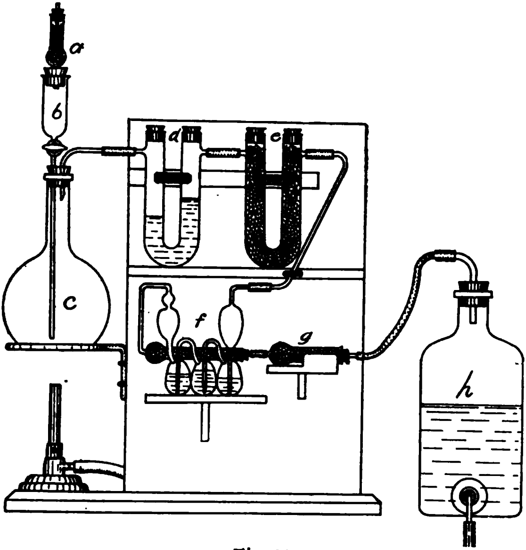

Fig. 14.

The Determination.

Weigh into the flask, *c*, from 2 to 10 grams of cement, triturate with water until all tendency to set has ceased, and connect the soda-lime tube *a* with the funnel tube. Aspirate a few liters of air through the apparatus, disconnect and weigh the potash bulb with its attached calcium chlorid tube. Again connect the apparatus, aspirate another two liters, and again weigh the potash bulb and attached calcium chlorid tube. If the first and second weights agree to within 0.0005 gram of each other, run into the flask 50 cc. of dilute hydrochloric acid and, if sulfids are present, a very little chromic acid. After connecting the bulb and tube in the train, and when action ceases apply heat gradually until the contents of the flask boil. Connect the soda-lime tube *a* and aspirate air slowly through the apparatus. Turn out the burner and aspirate two liters more of air. Disconnect the potash bulb and calcium chlorid tube and weigh. The gain in weight is carbon dioxid. Divide the increase by the weight of the sample used and multiply he quotient by 100, for the percentage of carbon dioxid in the cement.

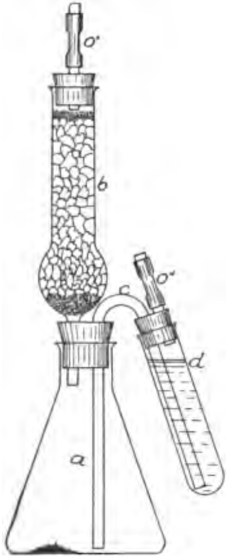

Fig. 15.

Rapid Determination

The Apparatus.

When rapid determinations of carbon dioxid have to be made, the following apparatus, which is a modification of Rose's form, may be used to advantage. It consists (Fig. 15) of a small 50 cc. Erlenmeyer flask, *a*, provided with a two-hole rubber stopper. Through one hole of this latter passes a 3 inch calcium chlorid tube, *b*, and through the other a piece of bent glass tubing, *c*, one arm of which reaches nearly to the bottom of the flask, the other through another stopper to the bottom of a small wide tube, *d*. This latter is made from a 5 inch test-tube. Such an apparatus will weigh from 35 to 60 grams according to the skill and choice of materials with which it is made.

Place a little wool or cotton in the bottom of the calcium chlorid tube and then fill the tube with calcium chlorid.

The Determination.

Next two-thirds fill the tube, *d*, with dilute hydrochloric acid, and weigh into the flask from 2 to 3 grams of Portland cement, or 1 to 2 grams of natural cement. Moisten the cement thoroughly with water, place the stopper in the flask, cap the openings, o' and o'', with pieces of rubber tubing closed at one end with bits of glass rod, and set in the balance case. After ten minutes weigh. Now attach a small guard tube, filled with calcium chlorid, to the opening, o', and after uncapping, o'', suck the acid from the tube, *d*, into the flask, *a*. As soon as the acid is all in *a*, close o'' with the finger and cap quickly. Remove the guard tube, and after effervescence ceases place the apparatus on a hot plate until the contents of the flask begin to boil. Remove from the hot plate, cap the opening, o', and set aside until the apparatus cools to the temperature of the room. Uncap o'', attach the guard tube to this opening this time, uncap o' and blow air gently through the apparatus for five to seven minutes. Cap the openings, place in the balance case and after ten minutes weigh. Always, before weighing, uncap either o' or o'' for a few seconds and then recap. This allows the pressure, caused by change of temperature, to adjust itself. The loss in weight represents the carbon dioxid, CO_2, in the cement. Divide the loss by the weight of the sample and multiply the result by 100 for the percentage.

Loss on Ignition

Weigh 2 grams of cement into a weighed platinum crucible, cover with a lid, and heat for five minutes over a Bunsen burner, starting with a low flame and gradually raising it to its full height. Then heat for fifteen minutes over a blast-lamp. Cool and weigh. The loss of weight represents the loss on ignition. This loss consists mainly of combined water and carbon dioxid driven off by the high temperature. Some chemists report, therefore, as "carbon dioxid and water," or having found the carbon dioxid, subtract the percentage from that of the "loss on ignition" and call the remainder "water of combination" or combined water.

Determination of Alkalies

(J. Lawrence Smith's Method)

Mix 1 gram of the finely ground cement with 1 gram of ammonium chlorid by grinding together in a clean agate mortar placed upon a sheet of black glazed paper. Add 8 grams of calcium carbonate free from alkalies, and transfer the mixture to a large platinum crucible provided with a closely-fitting cover. Heat, gently at first, over a Bunsen burner, then gradually raise the temperature to a full red heat and keep so for an hour. Cool the crucible, and if loose, transfer the sintered mass to a small beaker, or better a platinum dish. Wash the crucible and lid with hot water and pour into the dish or beaker. Digest the contents of the beaker until the sintered mass slakes to a fine powder.

If the sintered mass is not easily detached from the crucible, put the crucible into the beaker, add hot water and digest with heat until the mass slakes. Remove the crucible and wash it off into the beaker. Now filter into another platinum dish or beaker and wash the residue with water. Add 1.5 grams of pure ammonium carbonate, evaporate carefully to about 50 cc. and add a little more ammonium carbonate and a few drops of ammonia. Filter on a small filter into a dish of platinum or porcelain. Test the filtrate with a few drops of ammonium carbonate solution to make sure all the calcium has been precipitated. Evaporate to dryness and ignite at a barely visible red until all the ammonia salts are expelled and white fumes cease to come off. Cool, dissolve in a little water, add a few drops of ammonium carbonate solution and of ammonia, and filter from any residue that may form. Add three or four drops of dilute hydrochloric acid to the filtrate and evaporate to dryness in a weighed platinum dish. Ignite carefully as before and weigh as sodium chlorid and potassium chlorid, $NaCl + KCl$. Dissolve the mixed chlorids in water (they should be soluble without residue), and add to the solution an excess of platinic chlorid solution. Evaporate nearly to dryness on the water-bath, add 20 cc. of 80 per cent alcohol and let stand until the

the illustration. See that the poise R is at the zero mark, and balance the beam by turning the ball L.

Fill the hopper B with fine shot, place the specimen in the clamps N N, and adjust the hand wheel P so that the graduated beam D will rise to the stop K. Open the automatic valve J so as to allow the shot to run slowly into cup F. When the specimen breaks, the graduated beam D will drop and automatically close the valve J.

If the consistency of the cement is such that the specimen will not break before the beam strikes the valve, it will be necessary to stop the flow of shot and readjust the hand wheel. This can best be done by lifting the end of the beam against the stop by hand and tightening the hand wheel to hold the beam firmly in position. The shot is then to be allowed to run until the specimen breaks.

Remove the cup with the shot in it, and hang the counterpoise weight G in its place.

Hang the cup F on the hook under the large ball E, and proceed to weigh the shot in the regular way, using the poise R on the graduated beam D, and the weights H on the counterpoise weight G.

The result will show the number of pounds required to break the specimen.

The flow of shot can be regulated by the cut-off valve.

The Riehlé machine (Fig. 33) has all the weight upon one long graduated beam. The load is applied to the briquette by means of the lower hand wheel which actuates a worm gear, while the beam is kept in balance by a weight which is moved along the beam on a carriage by

Fig. 33.

the upper hand wheel. The upper lever serves as an indicator. In testing a briquette both wheels must be moved simultaneously so that the indicator vibrates in the center of its gate. In testing with this machine, the briquette is placed in the grips, and, being carefully adjusted, the hand wheel connected to the lower grip, is turned from

K_2SO_4 by multiplying by 0.35884. Multiply the result by 2 and subtract the weight of the $Na_2SO_4 + K_2SO_4$. The remainder represents the Na_2SO_4. Calculate the K_2SO_4 to K_2O by multiplying by 0.54057, and the Na_2SO_4 to Na_2O by multiplying by 0.43680. It must be borne in mind the fraction of the sample each precipitate represents in this scheme as the weight of silica should be multiplied by 100 and divided by the weight of the sample, while the lime should be multipled by 100 and divided by $\frac{2}{5}$ the weight of the sample for the per cent.

THE ANALYSIS OF CEMENT MIXTURES, SLURRY, ETC.

Since the success of cement-making depends primarily upon the proper portion of carbonate of lime to silica and alumina in the cement mixture, it is highly important to be able to rapidly estimate this ratio. If the materials from which the mixture is made are of normal constitution a determination in it of the calcium carbonate alone will suffice to check the correctness of the mixture.

For rapidly checking the percentage of calcium carbonate, two methods are in general use, the alkalimetric method in which the calcium carbonate is decomposed by a measured quantity of standard nitric or hydrochloric acid and the excess of acid determined by titration with standard alkali, and the indirect gas method in which the carbonate of lime is decomposed by acid and the evolved carbon dioxid gas collected in a suitable apparatus and measured; since the CO_2 is proportional to the $CaCO_3$, the percentage of lime can be calculated from the volume of CO_2. For the latter method the Scheibler's calcimeter is used. Neither of these methods gives very accurate results, and when the exact composition of the mixture is desired resort must be had to one of the longer gravimetic methods given further on.

When the slurry of the wet process is analyzed it should first be evaporated to dryness in a porcelain dish, then finely pulverized in a mortar and again dried for half an hour at 110°C. It will then be free from moisture and ready for analysis.

Rapid Methods for Checking the Percentage of Calcium Carbonate in Cement Mixtures

By Standard Acid and Alkali

Phenolphthalein.

Dissolve 1 gram of phenolphthalein in 100 cc. of alcohol (50 per cent). Keep in a small bottle provided with a perforated stopper through which passes a small pipette, made from a piece of 5 inch narrow bore glass tubing by drawing out one end to a fine opening. One drop of this solution is sufficient for a determination.

Standard $\frac{2}{5}$ N Sodium Hydroxid.

Weigh rapidly and roughly 20 grams of clean, bright, freshly cut metallic sodium. Cut in small pieces about the size of a pea, and keep in a small beaker of petroleum. Dry a piece of sodium between filter-papers and drop into a porcelain or silver dish containing from 250 to 500 cc. of freshly boiled, cold distilled water. When action ceases dry another piece of sodium and drop into the dish and repeat until all the sodium is dissolved. During the solution of the metal keep the dish covered with a watch-glass or an inverted funnel whose diameter is slightly smaller than that of the dish. When all the sodium has been dissolved, rinse off the funnel or watch-glass into the dish. Make up the solution to 2 liters, and keep in a tightly stoppered bottle.

Standard $\frac{2}{5}$ N Nitric Acid.

Take the specific gravity of the dilute nitric acid (1 : 1) used in the laboratory, by means of a hydrometer. Refer to the table in the appendix showing the strength of nitric acid of different densities and calculate from the seventh column what quantity of the dilute acid contains 50 grams of HNO_3. Measure out this volume carefully into a 2 liter graduated flask and dilute to the mark. Mix and preserve in a glass-stoppered flask or bottle.

Standardizing and Checking the Solution.

Measure with a pipette 50 cc. of the $\frac{2}{5}$ normal acid into a 250 cc. flask and add a few drops of the phenolphthaleïn indicator. Fill a burette with the $\frac{2}{5}$ normal alkali and run into the acid until a purple-red color is produced. Take the reading of the burette. Repeat this test until results agree closely. Grind finely in an agate mortar 20 to 25 grams of purest Iceland spar. Dry in an air-bath for one hour at 110° C. and keep in a glass-stoppered bottle. Weigh carefully 0.5 gram of this into the 250 cc. flask.

Provide the latter with a perforated stopper through which passes a glass tube 2 feet long drawn out to a small jet at the upper end. Measure into the flask 50 cc. of the $\frac{2}{5}$ normal acid and stopper tightly. When all action ceases place the flask still stoppered on the hot plate and heat to boiling for a few minutes. Remove from the source of heat, unstopper, reverse the glass tube, and rinse out into the flask. Add a few drops of phenolphthalein and titrate with the $\frac{2}{5}$ normal alkali until a purple-red color appears. Deduct the number of cubic centimeters required from that necessary to neutralize 50 cc. of the acid alone. The difference will be the number of cubic centimeters of standard alkali equivalent to 0.5 gram $CaCO_3$, or 0.28 gram of CaO. 0.28 divided by this difference will give the weight of calcium oxid equivalent to 1 cc. of the $\frac{2}{5}$ normal alkali.

Determination.

Weigh into the above-mentioned flask 1 gram of the cement mixture or dried slurry, add 50 cc. of $\frac{2}{5}$ normal acid from a burette or pipette and stopper the flask tightly with its perforated stopper. When action ceases place on the hot plate and boil briskly for a few minutes, remove, rinse out the tube, add phenolphthalein to the contents of the flask and run in the $\frac{2}{5}$ normal alkali until the solution turns rosy pink. Subtract the number of cubic centimeters required to neutralize the excess of acid from that required to neutralize 50 cc. of acid alone, multiply the difference by the CaO equivalent to 1 cc. of the alkali, the result multiplied by 100 will be the per cent of lime (CaO) in the mixture.

Notes

The process depends upon the decomposition of the calcium carbonate by a measured quantity of standard acid in excess of that required by theory.

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2.$$

Since the molecular weight of calcium carbonate is 100, and of nitric acid 63, 100 grams of $CaCO_3$ = 126 grams HNO_3; and as a liter of normal nitric acid contains 63 grams of HNO_3, 50 grams of $CaCO_3$ will require a liter of normal acid for its decomposition, or 2½ ($\frac{5}{2}$) liters, or 2,500 cc. of $\frac{2}{5}$ normal acid. Hence 0.5 gram of calcium carbonate would require $\frac{1}{100}$ of this volume or 25 cc. of $\frac{2}{5}$ normal nitric acid. The excess of nitric acid is then found by titration against $\frac{2}{5}$ normal alkali, using phenolphthalein or methyl orange as an indicator of the end of the reaction.

Phenolphthalein is a very delicate indicator. It is, however, very susceptible to carbon dioxid, and the solution must be freed from the latter by boiling whenever this indicator is used. It is also useless in the presence of free ammonia or its compounds. The addition of a few drops of the indicator to an acid or neutral solution shows no color, but the faintest excess of caustic alkali gives a sudden change to purple red. Methyl orange may be used in place of phenolphthalein. While not so delicate it possesses certain advantages over the latter. It can be used in the cold with carbonates, and its delicacy is not impaired by the presence of ammonia or its salts. A convenient strength for the methyl-orange indicator is 0.1 gram of the salt to 100 cc. of water. One drop of this solution is sufficient for 100 cc. of any colorless solution. Alkaline liquids are faintly yellow with methyl-orange and acid ones are pink.

Sodium hydroxid solution can be prepared from caustic soda itself instead of metallic sodium. The advantage which the latter has over the former is that it gives an alkali solution free from carbonate, and hence one with which phenolphthalein may be used as an indicator without boiling. Instead of the method from sodium described above the chemist may pursue the following plan of making the ⅖ normal alkali and use methyl-orange for an indicator.

First prepare the ⅖ normal nitric acid. Next dissolve about 44 grams of caustic soda in 2¼ liters of distilled water. Determine the strength of this solution by titration of 10 or 20 cc. against the ⅖ normal acid, and dilute the sodium hydroxid so that 1 cc. shall exactly neutralize 1 cc. of ⅖ normal acid. The number of cubic centimeters of water necessary to add to 2 liters of the potassium hydroxid solution in order to make it of such strength, may be found by the formula $\left(\frac{b}{a} - 1\right) \times 2,000$; when b = cc. of acid required to neutralize a cc. of soda.

Instead of ⅖ normal caustic soda the corresponding ⅖ normal caustic potash may be used. To prepare, substitute 55 grams of KOH for 44 grams of NaOH, and proceed as above.

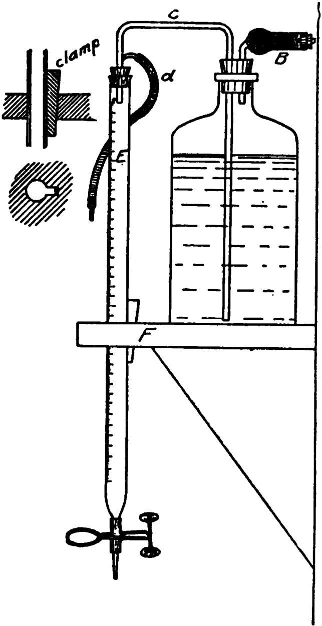

Fig. 16.

Fig. 16 shows a convenient apparatus for keeping the caustic soda solution. A is a 5 pint acid bottle resting upon a shelf over a table in a good light. The rubber stopper of the bottle contains two holes. Through one hole passes a calcium chlorid tube *B*, the bulb of which is filled with absorbent cotton. The tube itself is filled with soda-lime. The object of this tube is to free any air that may enter the bottle of its carbon dioxid and thus keep the solution free of carbonates. Through the other perforation in the stopper passes the long glass tube *c* bent in the form shown, and reaching to the bottom of the bottle. The other end of the tube passes inside a two-hole rubber stopper in the mouth of the burette and extends to the zero mark of the latter. The burette passes through a hole in the shelf and is held in position by a wedge. To fill the burette, suction is applied to the rubber tube *d*, which is connected with a short piece of glass tubing passing through the other perforation in the burette stopper. Since alkalies act on the glass stop-cocks of the ordinary burette causing them to stick, the old-style Mohr's form with its rubber connection, glass tip and pinch-cock is best for use with the alkali solution.

Instead of $\frac{2}{5}$ normal caustic alkali, $\frac{2}{5}$ normal carbonate may be used. Ignite pure dry sodium carbonate gently for fifteen or twenty minutes, cool in a desiccator and weigh quickly exactly 42.4 grams into a fairly large beaker. Dissolve in water and pour into a 2-liter graduated flask. Rinse out the beaker into the flask and dilute to the mark. Each cubic centimeter of this solution is equivalent to 0.0112 gram of lime, CaO. When this alkali is used with the acid it is unnecessary to standardize the solutions by the use of Iceland spar. Methyl-orange and *not* phenolphthalein must be used as an indicator with this solution.

The following is an example of the preparation of the $\frac{2}{5}$ normal nitric acid: The specific gravity of the nitric acid was found by the hydrometer to be 1.19; referring to the table of "Specific Gravities of Nitric Acid" in the index, 1 liter of acid of 1.19 sp. gr. contains 0.367 kilogram or 367 grams of HNO_3.

To find the quantity of acid containing 50 grams of HNO_3:

$$367 : 1000 :: 50 : x$$

$$x = 136.2 \text{ cc.} = \text{volume of 1.19 sp. gr. acid containing 50 grams } HNO_3.$$

Hence 136.2 cc. of the nitric acid were measured off into a two-liter flask and diluted to the mark,

Another way of preparing the acid is first to make up the ⅖ normal sodium carbonate solution as mentioned above. Then titrate 2 cc. of the dilute acid with the ⅖ normal sodium carbonate. Next calculate the quantity of acid which would be required to neutralize 2 liters of the latter, and after measuring this amount into a flask, dilute to 2 liters. This latter solution must be rechecked against the sodium carbonate.

To make acid and alkali agreeing with each other cubic centimeter for cubic centimeter, prepare 2¼ liters of acid a little stronger than ⅖ normal by either of the two methods just given (taking specific gravity on trial against ⅖ normal alkali), and determine its exact strength by duplicate tests against ⅖ normal sodium carbonate. Dilute this acid solution so that 1 cc. shall exactly neutralize 1 cc. of the sodium carbonate. The number of cubic centimeters of water it is necessary to add to two liters of the acid solution may be found by the formula $\left(\frac{b}{a} - 1\right) \times 2000$, where b = cc. of soda required to neutralize a cc. of acid. After dilution check the strength by titration against the ⅖ normal sodium carbonate.

Instead of nitric acid, hydrochloric acid may be used. Prepare the ⅖ normal hydrochloric acid similar to the ⅖ normal nitric acid, except as regards the quantity of acid. A liter of ⅖ normal hydrochloric acid should contain 14.6

grams hydrochloric acid to the liter. This solution may be standardized gravimetrically as follows:

To any convenient quantity of the acid to be standardized, add solution of silver nitrate in slight excess, and 2 cc. pure nitric acid (sp. gr. 1.2). Heat to boiling-point, and keep at this temperature for some minutes without allowing violent ebullition, and with constant stirring, until the precipitate assumes the granular form. Allow to cool somewhat, and then filter through asbestos. Wash the precipitate by decantation, with 200 cc. of very hot water, to which has been added 8 cc. of nitric acid and 2 cc. of dilute solution of silver nitrate containing 1 gram of the salt in 100 cc. of water. The washing by decantation is performed by adding the hot mixture in small quantities at a time beating up the precipitate well with a thin glass rod after each addition. The pump is kept in action all the time; but to keep out dust during the washing, the cover is only removed from the crucible when the fluid is to be added.

Put the vessels containing the precipitate aside, return the washings once through the asbestos so as to obtain them quite clear, remove from the receiver, and set aside to recover the silver. Rinse the receiver and complete the washing of the precipitate with about 200 cc. of cold water. Half of this is used to wash by decantation and the remainder to transfer the precipitate to the crucible with the aid of a trimmed feather. Finish washing in the crucible, the lumps of silver chlorid being broken down with a glass rod. Remove the second filtrate from the receiver and pass about 20 cc. of alcohol (98 per cent) through the precipitate. Dry at from 140° to 150°. Exposure for half an hour is found more than sufficient at this temperature, to dry the precipitate thoroughly. The weight of silver chlorid multiplied by 0.25424 gives the hydrochloric acid in the volume taken.

It will, in some laboratories, be found more convenient to make up ⅖ normal hydrochloric acid, standardize by precipitation with silver nitrate, and keep for use only in preparing and standardizing the ⅖ normal acid and alkali actually used. For example: 10 cc. of such a ⅖ normal hydrochloric acid solution gave, on checking with silver nitrate, 0.5751 gram silver chlorid.

A ⅖ normal solution should give $\left[\frac{(108 + 35.5) \times \frac{2}{5}}{100}\right]$ or 0.5740 gram AgCl. Hence the solution is a little above ⅖ normal strength, and a factor $\frac{0.5751}{0.5740}$ or 1.002 must be used with it. Ten cc. of a solution made by dissolving 16.5 grams of caustic soda in 1 liter, required 10.15 cc. of the above acid = 10.15 × 1.002 = 10.17 cc. of ⅖ normal. This made the value of 1 cc. of the alkali = 10.17 × 0.0112 ÷ 10 = 0.01139 gram of CaO. Wishing to prepare alkali of exactly ⅖ normal strength 38 grams of stick caustic soda were dissolved in 2½ liters of water. Ten cc. of this solution = 10.2 cc. of the ⅖ normal hydrochloric acid = 10.2 × 1.002 = 10.22 cc. of ⅖ normal, then using the formula $\left(\frac{b}{a} 1 - \right) \times 2{,}000$ given above, $\left(\frac{10.22}{10} - 1\right) \times 2{,}000 = 22$ cc. of water, were added to 2 liters (measured exactly) of the alkali. On again checking against the hydrochloric acid 10 cc. acid were required to neutralize 10 cc. of the alkali.

The Iceland spar may be obtained in a state of great purity, and is very well suited to standardizing the solutions. If the chemist has reason to fear impurities, dissolve 1 or 2 grams in a little dilute hydrochloric acid, evaporate to dryness, heat the residue in an air-bath at 110° C. for one hour, cool, redissolve in a little dilute hydrochloric acid and 50 cc. of hot water. Filter, wash, ignite, and weigh the residue of silica. To the filtrate add ammonia in slight excess, boil, filter, and wash. Ignite and weigh as $Fe_2O_3 + Al_2O_3$. The impurities should never exceed a few milligrams and may be deducted from the weight of Iceland spar. The difference will give, of course, the weight of $CaCO_3$, and this multiplied by 0.56 the weight of CaO.

The object of the long glass tube is that of a condenser to catch any volatilized acid. If it is rinsed out previous to use with little distilled water its efficiency is increased.

Instead of weighing 1 gram of the cement mixture, the factor weight may be used. That is such a weight that each cubic centimeter of the alkali will represent a per cent of CaO in the sample. To find this weight multiply the value of each cubic centimeter of the alkali in terms of grams of CaO by 100; the result will be the number of grams which should be taken. For example, suppose:

50 cc. acid = 49.1 cc. alkali.
50 cc. acid + 0.5 gram Iceland spar = 21.4 cc. alkali.

Then 0.5 gram $CaCO_3$ = 0.28 gram CaO = 49.1 − 21.4 = 27.7 cc. alkali, and 1 cc. alkali = $\frac{0.28}{27.7}$ = 0.01011 gram CaO.

Hence if we take 0.01011 × 100 = 1.011 grams cement mixture each cubic centimeter of alkali will be equivalent to 1 per cent of lime. If 50 cc. of the nitric acid were used and the excess of acid over what was required to decompose the 1.011 gram of cement mixture was 12.5 cc., then the mixture contains 49.1 − 12.5 = 36.6 per cent lime.

By Scheibler's Calcimeter

Fig. 17 shows the form of the calcimeter. It consists of the following parts:

Apparatus. 1. A small bottle, A, provided with a perforated stopper. In the bottle is placed a tube, *s*, of gutta-percha or glass.

2. Another bottle, B, provided with three openings in its neck. The right-hand opening of the bottle contains a firmly fixed glass tube which connects, on the one end with A by means of the flexible rubber tube, *r*, and on the other, inside of the bottle, B, with a very thin India-rubber bladder, K. The left-hand opening is controlled by a pinch-cock on a piece of rubber tubing slipped over the

glass tube, *q*. The central opening connects B with the measuring tube.

3. An accurately graduated glass cylinder, C, of about 150 cc. capacity.

4. Another glass cylinder, D, serving to regulate the pressure of the gas measured in C.

5. A water reservoir, E, consisting of a two-necked Woulff bottle. A glass tube, *p*, passes through a stopper in one neck nearly to the bottom of the reservoir and is connected with D by means of a piece of rubber tubing. The communication between D and E is controlled by means of a spring clamp.

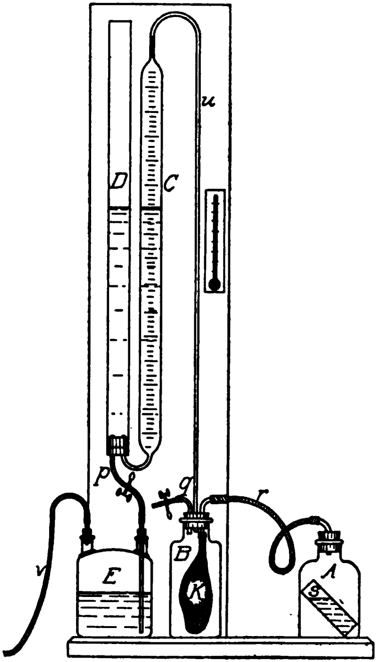

Fig. 17.

The whole apparatus with the exception of the first bottle, A, is fastened to a suitable stand by means of brass fittings and a thermometer is also attached.

Open the spring clamp, *p*, and pour distilled water into

D by means of a funnel until the bottle, E, is nearly full. When ready for a determination, remove the stopper from A, open the spring clamp, *p*, and blow air into *v* from the mouth until the level of the water in C and D reaches the zero point in the former. Care should be taken not to blow the water into the tube, *u*. If the level of the water passes the zero mark on C, it may be brought to the proper point by opening the spring clamp, *p*. The level in both tubes should be the same and stand exactly at the zero mark in C. The filling of the tube, C, will cause the bladder, K, to empty. If this does not happen, open the clamp, *q*, and blow air into B until the bladder flattens. If K is exhausted before C is filled the water in this latter tube will stand below that in D; in this case also open *q* until the levels are the same and at the zero point in C.

The Determination.

Place in the bottle, A, a weighed quantity of the dried slurry, cement mixture or limestone, in a finely powdered condition. Fill the cup, *s*, with 10 cc. of dilute (1 : 1) hydrochloric acid and place cautiously in A taking care not to spill any of the acid into the bottle. Stopper A tightly, greasing the glass stopper with a little tallow. This will cause the water in C to sink and in D to rise a little. Open *q* until the levels are the same, close and note the thermometer and barometer reading. Raise the bottle and tilt it slightly so that the acid in *s* runs into A, and gradually mixes with the sample. In doing this hold the bottle by the neck, to avoid warming, with the right hand and at the same time regulate *p* with the left so that the water in the two tubes is kept at the same height. Continue this operation until the water in C does not change its level for a few seconds. Now bring the columns of water in C and D to the same level and take the height in the tube, C, and note the reading of the thermometer to see if the temperature has remained constant.

Calculation of Results.

It is necessary as the first step to calculating the weight of calcium oxid equivalent to the volume of gas given off, to correct such volume for temperature, pressure, the tension of aqueous vapor and the gas absorbed or held back by the hydrochloric acid. This latter amounts to 7 per cent of the volume given off.[1] To make the necessary corrections use the formula

$$V = v \times \frac{100}{93} \times \left(\frac{1}{1 + 0.00367\,t} \times \frac{p - s}{760} \right)$$

in which

V = corrected volume (in cc.)
v = uncorrected volume (in cc.)
t = temperature, C°
p = pressure, mm. of mercury
s = tension of aqueous vapor at $t°$ C. as given in the table on page 98.

To find the weight of V cc. of carbon dioxid, multiply V by 0.0019712, the weight of 1 cc. of carbon dioxid, when measured at 0° C. and 760 mm. of mercury pressure. To convert this weight of carbon dioxid to its equivalent of lime, CaO, multiply this latter result by 1.2743; or to convert to calcium carbonate, $CaCO_3$, multiply by 2.2743.

---

[1] Warrington: Chem. News, 31, 253.

Or: Weight of CaO $= 0.002689 \times v \left(\frac{1}{1 + 0.00367\,t} \times \frac{p - s}{760}.\right)$

TENSION OF AQUEOUS VAPOR

t. Temp. °C.	s. Tension in mm. of mercury.	t. Temp. °C.	s. Tension in mm. of mercury.	t. Temp. °C.	s. Tension in mm. of mercury.
10	9.2	18	15.4	26	25.0
11	9.8	19	16.3	27	26.5
12	10.5	20	17.4	28	28.1
13	11.2	21	18.5	29	29.8
14	11.9	22	19.7	30	31.6
15	12.7	23	20.9	31	33.4
16	13.5	24	22.2	32	35.4
17	14.4	25	23.5	33	37.4

Notes

Tables are usually sold with these instruments which very much shorten the calculations, a graphic table such as the author describes in his "Chemists' Pocket Manual" would greatly simplify the calculations necessary with this instrument.

The above corrections for the volume of carbon dioxid may be done away with, by making a determination either with a standard sample of slurry or cement mixture or with pure calcium carbonate (Iceland spar) before each series of experiments with this instrument. If the temperature and pressure remain the same during the time for the series the result with the standard sample will give the relation between the volume of carbon dioxid and the weight of lime. For example, 0.5 gram of finely powdered Iceland spar ($CaCO_3$) was weighed out and the volume of carbon dioxid then measured and found to be 111.5 cc. 0.7 gram of the slurry, whose percentage of lime is desired, was next weighed out and the volume of gas found to be 116.5 cc. Now 0.5 gram of calcium carbonate is equivalent to 0.28 gram of lime. Then, volume of gas given off by the Iceland spar : that given off by the slurry :: weight of lime in Iceland spar : that in the slurry; or 111.5 : 116.5 :: 0.28 : x from which $x = 0.2927$, and per cent of lime in slurry $= \frac{0.2927 \times 100}{0.7} = 41.81$.

The apparatus should be placed where direct sunlight cannot fall upon it, and also be protected from any heating apparatus, such as radiator or stove, or Bunsen burner. It should also be stood near a North window so as to have sufficient light for reading and adjusting the water-levels.

The carbon dioxid in the slurry may also be determined by means of the apparatus shown on page 76. The determination is carried out similar to that of carbon dioxid in cement,[1] except that from 0.5 to 1 gram of slurry is sufficient for a sample. The loss of weight multiplied by 1.2743 gives the lime in the slurry.

Complete Analysis of Cement Mixture or Slurry

By Fusion with Sodium Carbonate

Weigh 1 gram of the finely ground dried cement mix-

---

[1] "Rapid Determination," page 76.

ture or slurry into a large platinum crucible and mix intimately with it by stirring with a smooth well-rounded glass rod from 5 to 10 grams of sodium carbonate and a very little sodium nitrate. Cover the crucible and heat gently at first over a low Bunsen flame, then gradually raise the latter until full heat is attained. Next heat over the blast-lamp until the contents of the crucible are in quiet fusion. Run the fused mass well up on the sides of the crucible and chill by dipping the bottom of the latter while red hot into a basin of cold water. When cold nearly fill the crucible with hot water and set on the hot plate for a little while. Pour the solution, and as much of the mass as becomes detached from the crucible, into a casserole or, better, a platinum dish. Again partly fill the crucible with water, and after digesting on the hot plate pour into the dish. Repeat this process until the mass has become thoroughly disintegrated. Half fill the crucible with dilute hydrochloric acid, heat and pour the acid into the casserole or dish, keeping as much of the latter as possible covered by a watch-glass to avoid loss by effervescence. Clean out the crucible with a rubber-tipped rod, and after acidifying the solution in the dish evaporate to dryness. Heat the dried mass in an air-bath at 110° C. for one hour, or on the hot plate or air-bath until it no longer gives off the odor of hydrochloric acid. Cool, moisten the dry mass with a few drops of dilute hydrochloric acid and a little water and again evaporate to dryness. Add 30 cc. of dilute hydrochloric acid,

Silica.

digest at a gentle heat for a few minutes and add 100 to 150 cc. of hot water. Allow to stand a little while on the hot plate and filter. Wash well with hot water, ignite over a Bunsen burner until all carbon is burned off, and then over a blast-lamp for five minutes. Weigh as impure SiO_2. Moisten the contents of the crucible with dilute sulfuric acid and half fill the crucible with hydrofluoric acid. Evaporate to dryness by placing over a burner in an inclined position in such a way that a low flame plays upon the under side of the crucible and the evaporation takes place only from the surface. Ignite and weigh. The difference between the two weights is silicon dioxid, SiO_2. If any appreciable residue remains in the crucible dissolve in a little concentrated hydrochloric acid and add it to the filtrate from the SiO_2.

Ferric Oxid and Alumina

Heat the filtrate from the silica, which should measure about 300 cc. to boiling, and add ammonia in slight but distinct excess; boil for a few minutes and allow the precipitate to settle. Filter and wash twice with boiling water. Remove the filtrate from under the funnel and in its place set the beaker in which the ammonia precipitation was made. Dissolve the precipitate of iron and alumina in a mixture of 15 cc. of dilute hydrochloric acid and 15 cc. of cold water, by pouring back and forth through the filter as long as any precipitate remains. Wash the filter-paper well with cold water, dry, place in a weighed platinum crucible and set aside. Reprecipitate the iron and alumina in the solution as before by heating to boiling and adding ammonia in slight but distinct excess. Filter, wash, and dry. Brush the precipitate from the filter upon a piece of glazed paper with a camel's hair brush, place the filter in the crucible with that from the first ignition and incinerate. When all the carbon is burned cool the crucible, set it upon another piece of glazed paper and brush the precipitate from the first paper into it. Ignite first over a Bunsen burner and then over a blast-lamp for four or five minutes. Cool and weigh as ferric oxid and alumina, $Fe_2O_3 + Al_2O_3$. To determine ferric oxid and alumina separately, determine the ferric oxid in this precipitate by one of the methods given in the scheme for the analysis of limestone, page 106, and deduct from the weight of the ferric oxid and alumina combined. The difference will be the weight of the alumina, Al_2O_3.

Lime.

Heat the filtrate from the iron and alumina to boiling and add 30 cc. of a saturated solution of ammonium oxalate. Stir and boil for a few minutes and allow to stand for some hours in order to allow the complete precipitation of the lime. Filter and wash once or twice. Dissolve the precipitate in a little hydrochloric acid, wash the filter-paper well with hot water and dilute the filtrate to 500 cc. Add ammonia to strongly alkaline reaction and then a little more ammonium oxalate. Heat to boiling. Allow to settle one hour, filter and wash. Dry and ignite over a blast-lamp until the weight is constant. Weigh as calcium oxid, CaO.

Make the first filtrate from the calcium oxalate precipitate slightly acid with hydrochloric acid, and add 30 cc. of sodium phosphate. Evaporate the solution to about 300 cc. and cool. Add ammonia drop by drop from a burette with constant stirring until the solution is slightly alkaline and the precipitate begins to form. Stop adding ammonia and stir for five minutes, then add one-tenth the volume of the liquid of strong ammonia and stir for five minutes more. Allow the solution to stand over night in a cool place, filter and wash with a mixture of 1000 cc. water, 500 cc. ammonia (sp. gr. 0.96), and 150 grams ammonium nitrate. Dry, ignite (do not use the blast-lamp), and weigh as magnesium pyrophosphate, $Mg_2P_2O_7$. Multiply this by 0.3619 for magnesium oxid, MgO.

Magnesia.

By Ignition with Sodium Carbonate

Place a clean dry agate mortar upon a large piece of glazed paper. Weigh roughly into it 0.5 gram of sodium carbonate, and after grinding this finely, weigh accurately 1 gram of the finely ground dried cement mixture or slurry and place with the sodium carbonate in the agate mortar upon the glazed paper. Mix thoroughly by grinding and then transfer the contents of the mortar to an ordinary size platinum ignition crucible. If any particles of the mixture have fallen upon the glazed paper either during the mixing or the transferring to the crucible, brush them also into the crucible, standing the latter, during the operation, on another piece of glazed

Silica.

paper. Cover the crucible with its lid and place over a Bunsen flame turned very low. Gradually raise this latter until the crucible is at a red heat. Keep at this temperature for from five to six minutes, and then heat over a good blast-lamp for ten or fifteen minutes. This treatment breaks up the silicates of alumina by the combined action of the lime in the cement mixture and the sodium carbonate at the high temperature of the blast-lamp, to form silicates and aluminates of calcium and sodium. Cool the crucible while still hot, by dipping in a basin of cold water and if the mass is in the form of a solid cake and loose from the crucible, transfer it to a 3½ inch casserole. Half fill the crucible with a mixture of 30 cc. of water and 10 cc. of dilute hydrochloric acid. Heat on a hot plate and then pour into the casserole, covering the latter with a watch-glass. Clean out the crucible with a rubber-tipped rod, using the rest of the mixture of acid and water. To the solution in the casserole add a few drops of concentrated nitric acid, evaporate to dryness and proceed as directed under the analysis of cements, page 24.

For the determination of sulfur trioxid, carbon dioxid, combined water, and alkalies, refer to the methods given under cement. The fusion method is to be preferred for determining sulfur trioxid.

THE ANALYSIS OF LIMESTONE

Determination of Silica, Ferric Oxid, and Alumina, Lime, and Magnesia

By Ignition of the Sample with Sodium Carbonate

Silica.

Weigh 1 gram of finely ground dried limestone into a platinum crucible and mix intimately with 0.5 gram of pure dry sodium carbonate by stirring with a glass rod. Place the crucible over a low flame and gradually raise this latter until the crucible is red hot. Continue heating for five minutes, then substitute a blast-lamp for the Bunsen burner and heat for five minutes longer. Place the crucible in a dish or casserole, add 40 cc. of water and 10 cc. of hydrochloric acid, and digest until all the mass is dissolved out of the crucible. Clean off the crucible inside and outside, add a few drops of nitric acid to the solution and evaporate it to dryness. Heat the residue at 110° C. for one hour, cool, add 15 cc. of dilute hydrochloric acid, cover with a watch-glass and digest for a few minutes on the hot plate. Dilute with 50 cc. of hot water, heat nearly to boiling, and filter. Wash the residue well with hot water. Dry, ignite, and weigh as silica, SiO_2.

Heat the filtrate to boiling, add ammonia in slight but distinct excess, boil for five minutes and filter. Wash the precipitate twice with hot water. Remove the filtrate from under the funnel and in its place stand the beaker in which the precipitation was made. Dissolve the precipitate in dilute hydrochloric acid and wash the filter-paper free from iron with cold water. Heat the solution to boiling and precipitate the iron and alumina with ammonia as before. Filter, allowing the filtrate to run into that from the first precipitation, wash well with hot water, dry and ignite. Weigh and report as ferric oxid and alumina.

Ferric Oxid and Alumina.

If the percentage of ferric oxid and alumina are desired separately, proceed as directed in A, B, or C.

A. Fuse the precipitate of ferric oxid and alumina, after weighing, with a little sodium carbonate, dissolve in a little water to which a few cubic centimeters of hydrochloric acid have been added, and drop into the solution a few small crystals of citric acid. Add ammonia until the solution smells slightly of the reagent, and then an excess of ammonium sulfid. Allow the black precipitate to settle, filter, wash a few times, dissolve in hydrochloric acid, add a little bromin water, boil a while and add ammonia in slight but distinct excess. Filter, wash well with hot water, ignite and weigh as Fe_2O_3. Deduct this weight from that of the total ferric oxid and alumina, for the weight of alumina, Al_2O_3.

B. Fuse the precipitate of ferric oxid and alumina, after weighing, with caustic potash in a silver crucible or dish. Treat the fusion with water, boil, filter, and wash. Dry, ignite, and weigh the residue as ferric oxid, Fe_2O_3. Deduct this weight from that of the ferric oxid and alumina, for the weight of alumina, Al_2O_3.

C. Dissolve the residue, after fusion with sodium carbonate, in a little dilute hydrochloric acid and determine the ferric oxid volumetrically by the method given on page 49.

Lime.

Heat the filtrate from the iron and alumina, which should measure between 750 and 1000 cc., to boiling and add 25 cc. of a saturated solution of ammonium oxalate. Stir and boil for a few minutes and allow the precipitate one hour in which to settle. Filter and wash well with hot water. After washing, treat the precipitate as directed below in *A*, *B*, or *C*.

A. Dry the precipitate by heating over a low flame, in a weighed platinum crucible, ignite until all carbonaceous matter is destroyed and ignite for fifteen minutes over a blast-lamp. Cool and weigh. Again ignite for five minutes over a blast-lamp and weigh. If this weight agrees to within 0.0002 gram of the former one it may be taken as the weight of the calcium oxid, CaO. If it does not agree, ignite again and repeat, if necessary, until the weight is constant.

B. Punch a hole in the filter-paper and wash the precipitate into the beaker in which the precipitation was formed. Wash the paper with dilute sulfuric acid from a wash-bottle and then with hot water. Dilute the solution to 300 or 400 cc., heat to 60° or 70° C., and after adding 10 cc. of dilute sulfuric acid titrate with permanganate. Calculate the per cent of lime, CaO, or calcium carbonate, $CaCO_3$, in the limestone, as directed under "Volumetric Determination of Calcium," page 40.

C. Dry the precipitate thoroughly, remove it as far as possible from the filter-paper to a piece of black glazed paper. Burn the filter-paper in a weighed crucible. Cool and add the precipitate. Drop concentrated sulfuric acid on the contents of the crucible until it is well moistened. Avoid adding an excess. Heat the crucible under a hood cautiously from a burner held in the hand until the swelling of the mass ceases, and the excess of sulfuric acid is driven off. This happens when white fumes cease to come from the crucible. Heat the crucible now for five minutes to a cherry-red heat, but do not use the blast-lamp. Cool and weigh as calcium sulfate, which multiplied by 0.41185 gives the equivalent of lime, CaO, or by 0.73504 that of calcium carbonate, $CaCO_3$.

Magnesia.

To the filtrate from the calcium oxalate add sufficient hydrochloric acid to make it slightly acid, and 30 cc. of sodium phosphate. Concentrate to about 300 cc. by evaporation. Set the solution in a vessel of cold water and when cooled to the temperature of the latter add ammonia, drop by drop,. from a burette, with constant stirring until slightly ammoniacal and the precipitate begins to form. Stop adding ammonia and stir for five minutes, add one-tenth the volume of the liquid of strong ammonia and continue the stirring for three minutes more. Allow the solution to stand in a cool place over night, filter, wash well with a mixture of 1000 cc. water, 500 cc. ammonia (sp. gr. 0.96), and 150 grams ammonium nitrate. Dry, ignite, and weigh as magnesium pyrophosphate, $Mg_2P_2O_7$. Multiply this by 0.36190 for its equivalent of magnesia, MgO, or by 0.75722 for magnesium carbonate, $MgCO_3$.

By Solution in Hydrochloric Acid

Insoluble Silicious Matter.

Weigh 1 gram of the finely ground dried limestone into a porcelain dish or casserole, cover with a watch-glass and add 30 cc. of water and 10 cc. of concentrated hydrochloric acid. Warm until all effervescence has ceased, uncover, add a few drops of nitric acid, and evaporate to dryness. Bake on the hot plate or sand-bath until all odor of hydrochloric acid has disappeared, or safer still, heat in an air-bath at 110° C. for one hour after the residue has become perfectly dry. Cool the dish and add 5 cc. of dilute hydrochloric acid, set on the hot plate, covered with a watch-glass for five minutes, then add 50 cc. of hot water and filter, after digesting until all except silicious matter dissolves. Wash thoroughly, ignite and weigh as "insoluble silicious matter."

Silica.

Should it be desirous to know the silica in the "insoluble silicious matter" fuse it with ten times its weight of pure dry sodium carbonate, first over a Bunsen burner turned low, and then, after slowly raising the flame of this latter to its full height, over a blast-lamp until the contents of the crucible are in a state of quiet fusion. Remove the crucible from the lamp and run the fused mass well up on its sides by tilting and revolving the crucible while held with the crucible tongs. While still hot dip the crucible three-quarters of the way up in a pan of cold water which will frequently cause the mass to loosen from the crucible. Wash off any material spattered on the crucible cover into a casserole or dish with hot water, and add the mass in the crucible if it has become detached. If not, fill the crucible with hot water and set on the hot plate until the fused mass softens and can be removed to the casserole. Dissolve any particles of the mass in hydrochloric acid, that adhere too firmly to the crucible to be removed by gentle rubbing with a rubber-tipped rod. When the hot water has thoroughly disintegrated the fused mass, cover the casserole or dish with a watch-glass and strongly acidify the contents with hydrochloric acid. Heat until all effervescence ceases and everything dissolves except the silica. Wash off the watch-glass into the dish and evaporate the solution to dryness. Heat for one hour at 110° C. in an air-bath, or on the hot plate at not too high a temperature until all odor of hydrochloric acid has disappeared from the dry mass. Cool, add 10 cc. of hydrochloric acid and 50 cc. of water, warm until all soluble salts are in solution, filter, wash well with hot water, dry, ignite, and weigh as silica, SiO_2.

Fe_2O_3, Al_2O_3, CaO, MgO.

Mix the two filtrates from the silica separations and proceed to determine iron and alumina, lime and magnesia, as directed in the method "By Ignition with Sodium Carbonate."

When the amount of sodium carbonate added to the "insoluble silicious matter" is greater than 0.5 gram, it is best in very accurate work, instead of mixing the two filtrates from the silica, to determine the iron, alumina, lime, and magnesia in each solution separately, since the large lime precipitate is almost sure to be contaminated with sodium salts if the two filtrates are mixed.

Determination of Organic Matter, Insoluble Silicious Matter, Ferric Oxid and Alumina, Lime and Magnesia

Organic Matter.

Weigh 1 gram of the finely ground dried limestone into a porcelain dish or casserole; cover with a watch-glass and add 30 cc. of water and 10 cc. of concentrated hydrochloric acid. Warm until all effervescence ceases, uncover and evaporate to dryness on a water-bath. Heat the dish for one hour, after the residue becomes thoroughly dry, at 110° C. in an air-bath. Cool the dish and add 5 cc. of hydrochloric acid and 50 cc. of hot water. Heat until all soluble salts dissolve, filter upon a Gooch crucible or a small counterpoised filter-paper. Wash well with hot water, dry at 100° C. in an air-bath and weigh as "organic matter" plus "insoluble silicious matter."

Now ignite until all carbonaceous matter is destroyed, and cool and weigh as "insoluble silicious matter." This weight subtracted from the preceding one gives the "organic matter." If the silica in the "insoluble silicious matter" is desired, fuse the latter with ten times its weight of sodium carbonate and proceed as described in the preceding scheme for the analysis of limestone "By Solution in Hydrochloric Acid."

Insoluble Silicious Matter.

Heat the filtrate from the "organic matter" and the "insoluble silicious matter" to boiling, add ammonia in slight but distinct excess, and proceed to determine the ferric oxid and alumina, lime and magnesia, as directed on page 105.

Fe_2O_3, Al_2O_3, CaO, MgO.

The Determination of Alkalies, Sulfuric Acid, Carbon Dioxid, Combined Water and Loss on Ignition

For the determination of these constituents refer to the methods given under cement.

METHODS FOR THE ANALYSIS OF CLAY

Determination of Silica, Ferric Oxid, Alumina, Lime and Magnesia

Silica.

Finely grind the sample of clay and heat at 100° to 110° C. for one hour in an air-bath. Transfer 1 gram of the dried clay to a fairly large platinum crucible. Mix with it by stirring with a smooth glass rod 10 grams of sodium carbonate and a little sodium nitrate. Heat over a Bunsen burner, gently at first, for a few minutes and then to quiet fusion over a blast-lamp. Run the fused mass well up on the sides of the crucible and allow to cool. Nearly fill the crucible with hot water and set on the hot plate for a few minutes. Pour the solution and as much of the mass as has become detached from the crucible into a casserole or better a platinum dish. Repeat this treatment until the mass has become thoroughly disintegrated. Treat what remains in the crucible with dilute hydrochloric acid and pour the acid into the casserole or dish. Clean out the crucible with a rubber-tipped rod and after acidifying with hydrochloric acid evaporate the contents of the casserole to dryness. Heat in an air-bath at 110° C. for one hour, or until all odor of hydrochloric acid has vanished. Cool, moisten the mass with dilute hydrochloric acid, add a little water and again evaporate to dryness. Now add 30 cc. of dilute hydrochloric acid, digest at a gentle heat for a few moments and add 100 to 150 cc. of hot water. Allow to stand a few minutes on the hot plate and filter. Wash the residue thoroughly with hot water, ignite over a Bunsen burner until all carbon is burned off, and then for five minutes over a blast-lamp, and weigh as impure silica. Moisten the silica with a few drops of dilute sulfuric acid and half fill the crucible with hydrofluoric acid. Evaporate to dryness by placing over a burner in an inclined position so that the low flame plays upon the side of the crucible and the evaporation takes place only from the surface. Ignite and weigh. The difference between the two weights is the silicon dioxid, SiO_2. If any appreciable residue remains in the crucible dissolve it in a little concentrated hydrochloric acid and add it to the filtrate from the silica.

Ferric Oxid and Alumina.

Heat the filtrate from the silica, which should measure about 300 cc., to boiling, and add ammonia in slight but distinct excess; boil for a few moments and allow the precipitate to settle. Filter and wash several times with hot water. Remove the filtrate from under the funnel and dissolve the precipitate of iron and alumina in a mixture of 15 cc. of dilute hydrochloric acid and 15 cc. of cold water, by pouring back and forth through the filter as long as any precipitate remains. Wash the filter-paper well with cold water, dry, place in a weighed platinum crucible, and set aside. Reprecipitate the iron and alumina in the filtrate as before by adding a slight but distinct excess of ammonia, filter, and wash thoroughly with hot water. Dry, transfer the precipitate from the filter to a piece of glazed paper with a camel's hair brush, place the filter in the crucible with the other filter-paper and ignite until all carbon is burned, cool the crucible, set it upon another piece of glazed paper and brush the precipitate from the first paper in with the filter ash, ignite first over a Bunsen burner and then strongly over a blast-lamp for four or five minutes. Cool and weigh as ferric oxid and alumina. Determine the ferric oxid in the precipitate as in *A* or *B* below and subtract the amount from this weight ; the difference will be the alumina.

A. Fuse the ignited precipitate with sodium carbonate, treat the fused mass with hot water and wash it out into a small beaker, allow the residue to settle and decant off the clear supernatant liquid through a small filter, leaving the residue in the bottom of the beaker. Wash the filter-paper once and pour a little hot concentrated hydrochloric acid through the filter into the beaker containing the residue. Heat gently, but do not boil. When all the residue is dissolved, determine the iron in the precipitate by reduction with stannic chlorid and titration with potassium bichromate as directed on page 49.

B. Brush the ignited precipitate into a small beaker, cover with a mixture of 6 cc. of water and 16 cc. of concentrated sulfuric acid, and covering with a watch-glass, digest on a hot plate or sand-bath until all dissolves, except possibly a residue of silica. Filter, if necessary, and determine the iron by reduction with zinc and titration with standard permanganate as directed on page 53.

Heat the filtrate from the iron and alumina to boiling

Calcium.

and add an excess of a saturated solution of ammonium oxalate. Stir and boil for a few minutes and set aside for several hours to allow the complete precipitation of the lime. Filter, wash, dry, and ignite over a blast-lamp until the weight is constant. Weigh as calcium oxid, CaO.

Magnesia.

To the filtrate from the calcium oxalate add sufficient hydrochloric acid to make it slightly acid and then 30 cc. of sodium phosphate. Concentrate the solution to about 300 cc. by evaporation and cool. Then add ammonia drop by drop from a burette, with constant stirring until the liquid is slightly ammoniacal and the precipitate begins to form. Stop adding ammonia and stir for five minutes, then add one-tenth the volume of the liquid of strong ammonia and continue the stirring for five minutes more. Allow the solution to stand in a cool place over night, filter, wash with a mixture of 1000 cc. water, 500 cc. ammonia (sp. gr. 0.96), and 150 grams ammonium nitrate. Dry, ignite (do not use the blast-lamp), and weigh as magnesium pyrophosphate, $Mg_2P_2O_7$. Multiply this by 0.36190 for magnesium oxid, MgO.

Notes

Clay is practically unacted upon by hydrochloric acid and requires fusion with alkaline carbonates for its decomposition.

Should the solution, on evaporation to dryness, show a tendency to climb the sides of the dish, greasing the latter lightly with vaseline or paraffine will remove the difficulty.

Mr. Thos. A. Hicks, of the Art Portland Cement Co., Sandusky, O., adopts the following method of fusion and solution where clays and slurries are under examination: One gram of the sample is fused with about ten times its weight of a mixture of potassium and sodium carbonates (1 : 1) in a platinum crucible over a blast-lamp. More of the fusion mixture is added and fused a little at a time until the crucible is one-half full of the fused mass. The crucible and contents are cooled by dipping in water and then dropped with the mouth downward on an iron plate covered with glazed paper. The fused mass is thus easily removed from the crucible. The mass is now brushed from the glazed paper into an evaporating dish and dissolved in dilute hydrochloric acid. The top of the dish is greased with vaseline to prevent "climbing" of the contents and the solution evaporated to dryness, after which it is heated at 110° C. in an air-bath until all free hydrochloric acid is driven off. The resulting mass is redissolved in water and dilute hydrochloric acid and the analysis completed as above, except that in the analysis of clay the precipitate of calcium oxalate is allowed to stand over night in order to secure as complete a separation as possible, and then titrated with standard permanganate.

The amounts of lime and magnesia in clays are small, so that the filtrate and washings from the second ammonia precipitation of the iron and alumina may be rejected and the lime and magnesia determined in the first filtrate only. For the same reason it is unnecessary to reprecipitate the calcium oxalate, although the solution is largely contaminated by sodium salts from the alkaline fusion.

Determination of Free, Hydrated and Combined Silica[1]

To ascertain how much of the silica found exists in combination with the bases of the clay, how much as hydrated acid, and how much as quartz sand or as a silicate present in the form of sand, proceed as follows:[2]

Let A represent silica in combination with the bases of the clay.

Let B represent hydrated silicic acid.

Let C represent quartz sand and silicates in the form of sand, *e. g.*, feldspar sand.

Dry 2 grams of the clay at a temperature of 100° C., heat with sulfuric acid, to which a little water has been added, for eight or ten hours, evaporate to dryness, cool, add water, filter out the undissolved residue, wash, dry, and weigh (A + B + C). Then treat it with sodium carbonate. Transfer it, in small portions at a time, to a boiling solution of sodium carbonate contained in a platinum dish, boil for some time and filter off each time, still very hot. When all is transferred to the dish, boil repeatedly with strong solution of sodium carbonate until a few drops of the liquid finally passed through the filter remain clear on warming with ammonium chlorid. Wash the residue, first with hot water, then (to insure the removal of every trace of sodium carbonate which may still adhere to it) with water slightly acidified with hydrochloric acid, and finally with water. This will dissolve (A + B) and

---

[1] Cairns' "Quantitative Chemical Analysis," page 68.

[2] Compare Fresenius' "Quantitative Analysis," 5th ed., 1865, § 236.

leave a residue (C) of sand, which dry, ignite, and weigh.

To determine (B), boil 4 or 5 grams of clay (previously dried at 100° C.) directly with a strong solution of sodium carbonate in a platinum dish as above, filter and wash thoroughly with hot water. Acidify the filtrate with hydrochloric acid, evaporate to dryness, and determine the silica as usual. It represents (B) or the hydrated silicic acid.

Add together the weights of (B) and (C), thus found, and subtract the sum from the weight of the first residue (A + B + C). The difference will be the weight of (A) or the silica in combination with the bases of the clay.

If the weight of (A + B + C) found here be the same as that of the silica found by fusion in a similar quantity in the analysis of the clay, the sand is quartz, but if the weight of (A + B + C) be greater, then the sand contains silicates.

The weight of the bases combined with silica to form silicates can be found by subtracting the weight of total silica found in 1 gram in the regular analysis, from the weight of (A + B + C) in 1 gram.

Notes

The following scheme is much less trouble than that described above and gives the silica present as sand and silicates undecomposable by sulfuric acid and that in combination with the alumina or combined silica.

Heat 1.25 grams of the *finely* ground and dried(at 100° C.) clay with 15 cc. of concentrated sulfuric acid to near the boiling-point of the acid and digest for from ten to twelve hours at this temperature. *Cool*, dilute and filter. Wash and ignite the residue to a constant weight. Call this weight A. After weighing brush the residue which consists of silica present as sand and undecomposable silicates and silica from the decomposition of the silicates of alumina, into an agate mortar, grind very finely and weigh 0.5 gram of it into a platinum dish containing 50 cc. of *boiling* caustic potash solution (of 1.125 sp. gr.). Boil for five minutes, filter, wash, first with hot water and then with water containing a little dilute hydrochloric acid and then again with hot water, dry and ignite to a constant weight. Call this weight B. Multiply A by 0.4 (to correct the 1.25 grams of clay used to correspond to the 0.5 gram of the residue taken for treatment with caustic potash solution) and subtract B from the product. Multiply the difference by 200 for the per cent of silica combined with alumina in the clay. This deducted from the total silica found by analyses gives the silica as sand and undecomposable silicates.

Determination of Water of Combination

Should the clay contain very little organic matter, iron pyrites or calcium carbonate, heat 1 gram of the previously dried cement for twenty minutes to a bright redness over a Bunsen burner. The loss in weight will represent the water of combination. If, however, the clay contains much organic matter, calcium carbonate or iron pyrites, the wear of combination should be determined by absorption in a weighed calcium chlorid tube as described for cement analysis on page 64.

Note

If calcium carbonate is present, weigh 1 gram of clay into a beaker, add 50 cc. of water and 2 or 3 cc. of dilute hydrochloric acid. Warm gently until the carbon dioxid is expelled and filter through a weighed Gooch crucible and felt, or upon a previously weighed ashless filter. Wash, dry for two hours at 100° to 105° C. and weigh. Ignite the filter and residue strongly and again weigh. The loss represents water of combination (and organic matter if present). If a filter-paper has been used its weight should of course be added to the weight of residue after ignition before subtraction.

Many chemists simply heat 1 gram of dried clay over a blast for twenty minutes reporting the loss of weight as *loss on ignition*. This loss, of course, comes from combined water and carbon dioxid driven off (from the decomposition of carbonates), organic matter burned and iron pyrites changed from iron sulfid, FeS_2, to ferric oxid.

Sulfur and Iron Pyrites

For the determination of sulfur in clay, proceed as directed for determining this constituent in cements by fusion with sodium carbonate and potassium nitrate. Multiply the weight of barium sulfate by 0.25845 and report as iron pyrites, FeS_2, or by 0.13734 and report as sulfur.

PHYSICAL METHODS

SPECIFIC GRAVITY

With Le Chatelier's Apparatus.

The specific gravity of cement is usually taken by means of Le Chatelier's apparatus, which has lately been recommended by the French Commission des Méthodes d'Essai des Matériaux de Construction. Referring to Fig. 18 it will be seen to consist of a flask of 80 cc. capacity, having a neck about 20 cm. long and about 9 mm. in diameter. About half way up the neck is a bulb of exactly 20 cc. capacity between the marks indicated in the illustration. Commencing at the upper of these two marks, the tube is graduated from 0 to 5 cc. in tenths of a cubic centimeter. The method of using the apparatus is as follows: The flask is filled to the lower mark of the 20 cc. bulb with paraffin, turpentine or benzine. This latter should be free from water and not very volatile or hygroscopic. Weigh out next exactly 64 grams of cement and introduce into the neck of the flask by means of a funnel. The funnel stem should reach below the 0 graduation on the stem, so that should any of the cement fall against the side of the neck it will be below the space eventually occupied by the liquid. The cement is added cautiously towards the last until the para-

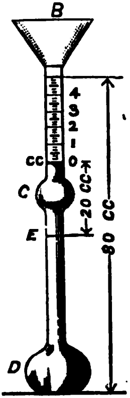

Fig. 18.

ffin or benzine rises to the zero mark on the neck above the bulb. The remainder of the cement is then weighed, and from this the quantity of cement which displaced 20 cc. is calculated by difference. Instead of the above method, the operator may add the entire 64 grams of cement. The reading on the neck plus 20 will give the number of cubic centimeters displaced by 64 grams of cement. To find the specific gravity in either of the above cases divide the weight of the cement taken by the volume of liquid displaced, the result will be the specific gravity of the cement. The flask during the operation should be either kept in a vessel of water or immersed a short while before each reading in order to guard against errors from variations in the volume of benzine due to temperature.

With the Schumann-Candlot Apparatus.

Another form of apparatus in frequent use, particularly abroad, for taking the specific gravity of cement is that of Schumann as modified by Candlot. This apparatus (Fig. 19) consists of a graduated tube, B, terminated by a bulb, A. This tube fits tightly on the flask, D, by means of a ground joint. To

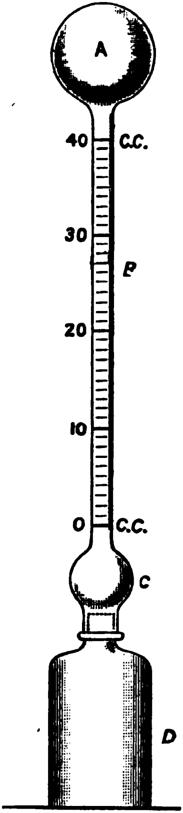

Fig. 19.

use the apparatus, paraffin, turpentine, or benzine is introduced into the detached and inverted tube B in sufficient quantity to bring the level of the liquid above the zero point on the tube when the latter is in position on the flask D. A note is then made of this point, the tube is inverted and the flask detached. Into the latter is then introduced a known weight (usually 100 grams) of cement, and the flask is again connected with the tube. The whole apparatus is now agitated to expel air bubbles, then set in an upright position and the new height to which the liquid rises is read. The difference between this height and the last is the volume of liquid displaced by the cement. To find the specific gravity of the cement divide the weight of cement taken by the volume displaced, the result will be the specific gravity.

Where the apparatus is not at hand for the above methods, the specific gravity may be taken by means of the ordinary specific gravity bottle. First weigh the bottle empty then fill the bottle with water and weigh, then dry and fill with benzine and weigh. Calculate the specific gravity of benzine from the formula

With the sp. gr. bottle

$$x = \frac{B - p}{W - p},$$

where x = sp. gr. of benzine, B = weight of bottle full of benzine, W = weight of bottle full of water, and p = weight of the empty bottle.

Now introduce a weighed portion of the cement into the bottle, fill with benzine, and weigh. The specific gravity of the cement may then be found by the formula

$$X = \frac{C \times x}{B + C - D},$$

where B = weight of the bottle full of benzine, C = weight of the cement. D = weight of the bottle and the cement and the benzine, x = specific gravity of the cement as found above, and X = specific gravity of the cement. Turpentine or paraffin may be used in place of benzine.

FINENESS

Importance of Fineness.

The fineness to which cement is ground is an important point. Since cement is usually used with sand, the strength of the mortar increases with the fineness of the cement, because the greater is the covering power of the cement, *i. e.*, the more parts of cement come into action with the sand. A test for fineness is nearly always included in cement specifications, as the indications from a fair degree of fineness coupled with proper tensile strength, neat, are that the cement will give good results when used with sand. The Committee on Uniform Cement Tests of the American Society of Civil Engineers recommended in their report that three sieves should be used in making the fineness test, having 2,500, 5,774, and 10,000 meshes per square inch respectively. The size wire used in these sieves is very important since it regulates the size of the opening. The 2,500 mesh should be made of No. 35, the 5,774 of No. 37, and the 10,000 of No. 40 wire, Stubbs' wire gauge.

In making this test, it is usual to take 100 grams and after sifting until no further appreciable quantity can be shaken or rapped through the sieve, weighing the residue caught by the sieve. The weight of this residue in grams represents the percentage of cement retained by that particular sieve. It is usual where the specifications call for a test with more than one sieve to start with the finest, and then after weighing treat the residue caught upon this with the next size in point of coarseness, etc., until the coarsest has been used. The metal-framed sieves with top and bottom are most convenient for this test. They can also be obtained in nests of any desired size and number. Fig. 20 shows a form of mechanical shaking sifter, manufactured by the Riehlé Bros. Testing Machine Co. In these nests of sieves the coarsest should be at the top and the finest at the bottom. To the weight of the residue on each sieve is to be added the weight of that caught on all the sieves above it.

Method of Making the Test.

SETTING PROPERTIES

The rapidity with which a cement sets furnishes us with no indication of its strength. The test is usually made to determine the fitness of the material for a given piece of work. For example, in most submarine work a quick-setting cement is desired, that is, a cement which loses its plasticity in less than half an hour, while for most purposes where sufficient time will be given the cement to harden before being brought into use, a slow-setting cement will

Value of the Test.

usually answer better, or one that sets in half an hour or more. The slow-setting cements can be mixed in larger quantities than the quick setting, and do not have to be handled so quickly, so that for most purposes where permissible they are used.

Fig. 20.

The test proposed by General Gilmore, U. S. A., for determining setting properties is the one most used in this country. It consists in mixing cakes of neat cement from 2 to 3 inches in diameter and 1/2 inch thick to a stiff plastic consistency and observing the time when they will bear a needle 1/12 inch in diameter weighted with 1/4 pound. This is noted as the beginning of the set. These pats should be made with a flat top so as not to catch the edge of the needle. Trials are next made every now and then with a 1/24 inch in diameter needle weighted with one pound. The time at which the cake is sufficiently firm to bear this latter needle is noted as the end of the set. Fig. 21 shows the two Gilmore wires or needles. It is best to have the needles supported in a rack, as shown. They will then bear perpendicularly and evenly upon the top of the pat. The water with which the pat is gauged should be from 60° –70° F., and the pat placed in air of the same temperature.

Method of Making the Test.

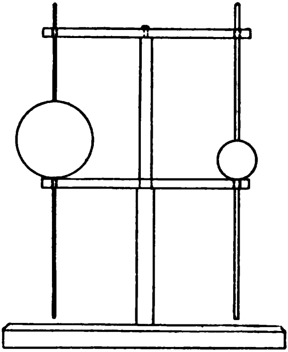

Fig. 21.

In order to determine the time of set of slow-setting cements by the official German method (cements which set in two hours or more are called slow setting in Germany), take a sample of neat cement and mix for three minutes with water

German Method.

to a stiff paste; for quick-setting cements only one minute's mixing is required. The mixture is then spread on a glass plate, at a single operation, in the form of a pat 1 1/2 cm. thick (about 5/8 inch), and tapering towards the edges. The consistency of the gauged cement should be such that a few taps on the glass plate will cause the mass, which was placed thereon with a spatula, to flow outwards towards the edges. From 27 to 30 per cent of water is generally sufficient for the purpose. When the pat becomes hard enough to withstand a slight pressure with the finger nail, the cement may be considered as set.

The above methods are accurate enough for practical purposes.

With the Vicat Needle.

Where more accurate determinations for experimental purposes or particularly to determine the beginning of the set, as this point is important as determining the time before which the cement should be used since it should not be disturbed after the set has begun, the Vicat needle is most used. This is the apparatus adopted by the Association of German Cement Manufacturers and also the French Commission des Methodes d'Essai des Materiaux de Construction. The Vicat needle (Fig. 22) consists of a frame K, in which moves a rod, L. Over the upper end of this rod may be slipped either of two caps, D (shown on the needle) or A; and in its lower end may be fixed, by a thumb-screw, G, either a needle, H, having a cross-section of one square millimeter, or a plunger, B, 1 centimeter in diameter. The rod is held in any desired position in the frame by the thumb-screw, F. The rod carries an indicator, E, which moves up and down a scale on the frame and shows the position of the rod. The weight of the rod, L, with either the cap, D, and needle, H, or the cap, A, and the rod, B, is 300 grams. The paste of cement to be tested is held in a rubber ring 8 cm. clear diameter and 4 cm. high, resting on a glass plate, J. The cement to be tested is mixed with water to a plastic consistency, and filled into the rubber ring level with the top. This is then immediately placed under the rod, the latter having the plunger, B, and cap, A. If the plunger penetrates the mortar to a distance of 6 mm. from the bottom, the mortar is of the proper consistency for the test. The needle, H, and cap, D, are now substituted for the plunger, B, and cap, A. Trials are then made every ten minutes and the time when the needle first refuses to entirely transverse the mortar in the ring is noted as the beginning of the set, while the time at which the needle gently applied to the surface of the mortar rests upon it and does not perceptibly penetrate into it, is said to be the end of the set.

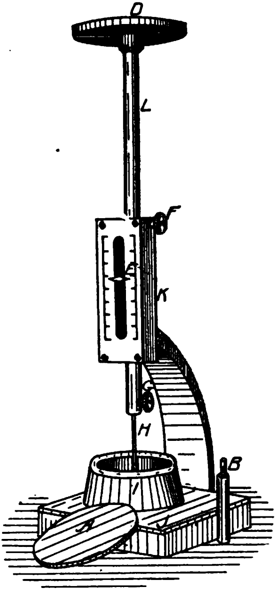

Fig. 22.

TENSILE STRENGTH

While in actual work cement is never used in such a way as to subject it to tensile stress, still the most usual test for cement is that of the tensile strength. This test is one largely of convenience. A tensile stress can be more easily applied and with a less expensive machine than can a compressive one, and as the ratio between the tensile and compressive strength of a cement has been found to be a fairly constant one, the greater the tensile stress a cement will stand the greater in general will be its compressive strength.

In applying the tensile strength test to a cement, briquettes are made of the neat sample, or of any desired proportion of cement and sand, by mixing with sufficient water to form a very stiff paste and then pressing into moulds, having a definite cross-section at the middle. At the expiration of a certain length of time the briquettes are pulled apart by means of a machine designed for that purpose and the number of pounds stress required to do this is recorded as the tensile strength of the cement.

Briquettes.

Fig 23 shows the form of briquette recommended in the report of the committee on a uniform system for tests of cement of the American Society of Civil Engineers,[1] which is now the standard in this country, and Fig. 24, the form recommended by the Association of German Cement Makers, which is the standard in Ger-

---

[1] This committee presented its report at the annual meeting of the society January 21, 1885, and was then discharged. A new committee has since been appointed, but has as yet made no report.

many. The dimensions of the two forms are given in the drawings. As will be seen, the weakest section of briquettes of either form is at the center and is one inch in cross-section, in the case of the United States standard; and 5 square centimeters in that of the German. Comparative tests show the American standard to give the higher result of the two. In the case of briquettes of neat cement, this difference amounts sometimes to as much as 30 or 40 per cent of the lower.

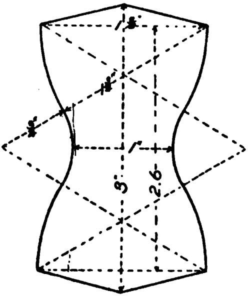

Fig. 23.

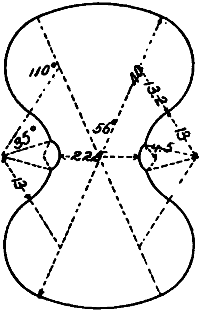

Fig. 24.

The briquettes to be broken at the expiration of twenty-four hours are made of neat cement, that is, cement alone, while those to be broken only after the lapse of seven days or longer, should be made either of neat cement or in the case of Portland cements of a mixture of one part cement to three parts sand, and in the case of natural cements of equal parts cement and sand.

Molds.

The various kinds of molds used in this country for making briquettes are shown in Figs. 25, 26, and 27. They are usually made of gun metal or some alloy of copper that does not easily rust on exposure to moisture. They are usually in two pieces to facilitate the removal of the briquette after molding. When in use the two sections are held together by means of a clamp provided with a thumb-screw as shown in Fig. 26, or by a spring as in Fig. 27. Preference is usually to be given to the clamp rather than to the spring, as the latter is likely to give a little during the ramming of the mortar into the mold, allowing the mold to spread, which would result in a distorted briquette, and an enlarged breaking section. Beside the single molds shown above, molds are upon the market holding more than one briquette. Fig. 28 shows such a "gang mold." Single molds are supposed to give higher results than gang molds.

Fig. 25.

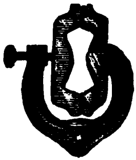

Fig. 26.

Fig. 27.

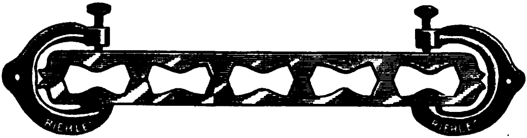

Fig. 28.

After use the molds should be wiped with a cloth and a little machine oil. This not only helps to keep the mold, but also to facilitate the subsequent removal of the briquette.

Sand.

The sand recommended by the report previously referred to of the committee of the American Society of Civil Engineers, should be the crushed quartz used in the manufacture of sand paper. As this sand is a commercial product it can be obtained in large quantities and of standard grades. The crushed quartz should be of such size that it will all pass a No. 20 sieve and yet be retained upon a No. 30.

Where the value of the cement is desired with regard to some particular piece of work, the sand used for the test may be the sand that is to be used for the work. In this case it is the mortar that is tested rather than the cement. Just as a series of tests made with a standard sand and various brands of cement would give the comparative value of the cements, so a series of tests with an established brand of cement and various sands will give the comparative value of the sands.

Making the Briquettes.

Two general methods are employed for making the mortar for the briquettes: The plastic method used in England, France, and the United States, and the dry method, which is the standard method of the Association of German Cement Manufacturers. The dry method probably in most cases gives greater uniformity of result than the plastic. The latter, however, agrees more closely with the conditions of the use of the material in actual practice. The committee of the American Society of Civil Engineers have adopted the following rule for making their briquettes:

"The proportion of cement, sand, and water should be carefully determined by weight, the sand and the cement mixed dry, and the water added all 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 a trowel, without ramming, and struck off level; the mold in each instance while being charged and manipulated to be laid directly on glass, slate, or some other non-absorbing material.

"The molding must be complete 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."

The Association of German Cement Manufacturers have adopted the following specification for making the briquettes by hand:

"On a metal or thick glass plate five sheets of blotting-paper soaked in water are laid, and on these are placed five molds wetted with water. 250 grams of cement and 750 grams of standard sand are weighed and thoroughly mixed dry in a vessel; then 100 cc. of fresh water are added and the whole mass mixed for five minutes. With the mortar so obtained the molds are at once filled, with one filling so high as to be rounded on top, the mortar being well pressed in. By means of an iron trowel, 5 to 8 cm. wide, 35 cm. long, and weighing about 250 grams, the projecting mortar is pounded, first gently and from the sides, then harder into the molds, until the mortar grows elastic and water flushes to the surface. A pounding of at least one minute is necessary. An additional filling and pounding of the mortar is not admissible, since the test pieces of the same cement should have the same density at the different testing stations. The mass is now cut off with a knife and the surface smoothed. The mold is carefully taken off and the test-pieces placed in a box lined with zinc, which is to be provided with a cover to prevent a non-uniform drying of the test-pieces at different temperatures."

For making test-pieces of neat cement:

"The inside of the molds are slightly oiled, and the same are placed on a metal or glass plate without blotting-paper. 1000 grams of cement are weighed out, 200 grams of water added, and the whole mass thoroughly mixed for five minutes. The forms are well filled and then proceed as for hand-work with sand mortar."

Mixing the Mortar.

The mortar for the briquettes should be mixed upon some non-absorbent substance such as a slab of slate or a plate of glass. If the plastic method is used, the quantity of water used should be just sufficient to make the mass of about the consistency of stiff plasterers' mortar. The proportion of water to cement varies with the fineness, age, etc., of the cement, and also upon the temperature of the air and water. An approximate quantity for briquettes of neat Portland cement is 25 per cent; for those of neat natural cement, 30 per cent; for briquettes of one part sand and one part cement, 15 per cent; and for those of one part cement and three parts sand, 12 per cent; of the total weight in either case of the sand and cement. The percentage of water for any given cement may readily be found, by placing a small weighed portion of it, say 100 grams, upon the mixing slab and adding water from a graduated cylinder until the mass is of the desired consistency. Note is then taken of the quantity required.

The consistency of mortar does not depend entirely upon the quantity of water used, but also upon the manner and the extent of working the mortar in gauging. In the French and the German standard specification it is required that the mortar shall be worked for five minutes.

Hardening the Briquettes.

The molds should be set upon some level, smooth, nonabsorbent material such as a glass or slate slab, and the molding must be complete before incipient setting begins. As soon as the briquettes are hard enough to bear it they should be taken from the molds and kept moist by covering with a damp cloth or placing in a moist closet until they are immersed. The moist closets are made of tin or zinc similar in shape to the air-bath described on page 18, and are of sufficient size to meet the requirements of the laboratory in which they are to be used. The air in them is kept moist by a layer of water upon the bottom, or by a moist sponge. The briquettes are placed upon glass or metal shelves above the surface of the water. Mr. Richard L. Humphrey, in the Proceedings of the Engineer's Club of Philadelphia, November, 1896, describes a soapstone moist closet which he used in the cement testing laboratory of the city of Philadelphia. For the sake of uniformity, the briquettes both of neat cement and those containing sand are recommended by the committee of the American Society of Civil Engineers to be immersed at the end of twenty-four hours, except in the case of one-day tests, where they are immersed as soon as set. Ordinary fresh clean water, having a temperature of from 60° to 70° F., should be used for the water of both mixing and immersion. 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 briquette and of the testing room should be constant, between 60° and 70° F.

The briquettes may be placed in water either flat or on edge. The latter gives more surface exposed to the water. The tanks in which the briquettes are immersed may be made of galvanized iron and of any desired size. They are usually, however, from two to three inches deep. Where space is limited, they may be placed one above the other on a suitable framework.

Clips.

The various forms of clips are shown in the following illustrations. Fig. 29 shows that recommended by the American Society of Civil Engineers. This latter form does not seem to be very satisfactory as the bearing surface is insufficient and the briquette is likely to break from the crushing of its surface at the point of contact. Fig. 30 is probably more to be preferred. It affords sufficient bearing surface without binding. Various authorities at different times have advocated cushioning the grips by placing blotting paper between jaw of the grip and the briquette, or stretching rubber bands around the jaws, so as to soften the point of contact of these with the test piece. Mr. W. R. Cock[1] has devised the use of a rubber bearing as shown in Fig. 31. In this clip the line of contact between the grip and the briquette is a rubber tube mounted on a pin. These tubes are readily replaced for a few cents when worn out. Adjustable and roller clips are also upon the market and seem to give satisfaction. In order that the stress upon the briquette shall be along the proper lines great care must be exercised in properly centering the briquette in the clips, and the form of the latter must

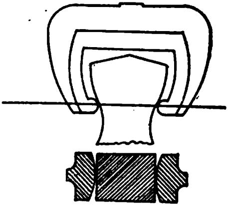

Fig. 29.

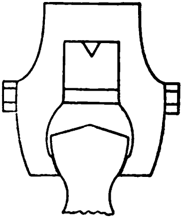

Fig. 30.

Fig. 31.

---

[1] Eng. News, Dec. 20, 1890.

be such that it does not clamp the head of the briquette thus preventing the test piece from adjusting itself to an even bearing. At the same time the surface of contact must be sufficient to prevent the briquette from being crushed at this point. Striking the happy medium has so far proved not any too easy. The clips are usually suspended by conical bearings which permit them to turn so as always to transmit the stress in a direct line between the bearings.

Cement Testing Machine.

Of the various testing machines in use, the Michaelis machine is almost universally used in Germany, while in this country the Fairbanks (which is practically the same as the Michaelis) the Riehlé and the Olsen are most used.

The Michaelis[1] double-lever, automatic machine for testing cement is described as follows: Upon a massive pillar, about one foot in height, are fastened two levers, connected with one another; the upper has a leverage of 10 to 1 and the lower of 5 to 1. To the latter is fastened the upper clip; the lower clip is attached by means of a ball point to a screw with a hand wheel for lowering or raising. There is also a counter balance for bringing the levers into exact equilibrium. The weight is applied by means of a stream of shot flowing into a bucket attached to the upper lever. The moment the specimen breaks, the bucket drops striking a lever below which closes a trap and shuts off the stream of shot instantly. The shot in the bucket is then weighed upon a spring or other form of

---

[1] Gary: Trans. Am. Soc., C. E., 30, 26.

scale. This weight, multiplied by 10, gives the breaking strain per centimeter when the German form of briquette is used.

The Fairbanks cement testing machine (Fig. 32) is in principle the same as the Michaelis. It differs, however, much in form of construction. In this machine the weight of the shot is determined on hanging the bucket on the opposite end of the lever used for breaking the specimen, by means of a sliding poise. To operate the machine:

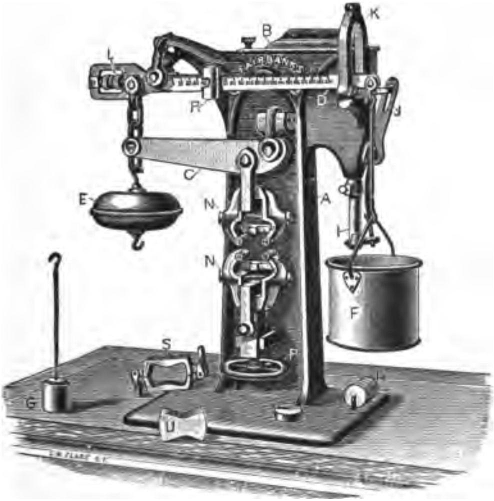

Fig. 32.

Hang the cup F on the end of the beam D, as shown in the illustration. See that the poise R is at the zero mark, and balance the beam by turning the ball L.

Fill the hopper B with fine shot, place the specimen in the clamps N N, and adjust the hand wheel P so that the graduated beam D will rise to the stop K. Open the automatic valve J so as to allow the shot to run slowly into cup F. When the specimen breaks, the graduated beam D will drop and automatically close the valve J.

If the consistency of the cement is such that the specimen will not break before the beam strikes the valve, it will be necessary to stop the flow of shot and readjust the hand wheel. This can best be done by lifting the end of the beam against the stop by hand and tightening the hand wheel to hold the beam firmly in position. The shot is then to be allowed to run until the specimen breaks.

Remove the cup with the shot in it, and hang the counterpoise weight G in its place.

Hang the cup F on the hook under the large ball E, and proceed to weigh the shot in the regular way, using the poise R on the graduated beam D, and the weights H on the counterpoise weight G.

The result will show the number of pounds required to break the specimen.

The flow of shot can be regulated by the cut-off valve.

The Riehlé machine (Fig. 33) has all the weight upon one long graduated beam. The load is applied to the briquette by means of the lower hand wheel which actuates a worm gear, while the beam is kept in balance by a weight which is moved along the beam on a carriage by

Fig. 33.

the upper hand wheel. The upper lever serves as an indicator. In testing a briquette both wheels must be moved simultaneously so that the indicator vibrates in the center of its gate. In testing with this machine, the briquette is placed in the grips, and, being carefully adjusted, the hand wheel connected to the lower grip, is turned from left to right, and continued until the indicator of weighing beam (which moves in a gate at the top of the machine and nearly on a line with the eye of the operator) drops. This indicator moves the reverse of the weighing beam, and when too much strain is exerted it falls, and when too much weight is applied it raises to the top of the gate. It is important that the indicator should vibrate in the center of the gate, and rest neither up nor down. This result can be attained by carefully manipulating the large hand wheel and the simultaneous movement of the poise on the weighing beam. When the indicating beam drops down, when the test first begins, the rest of the test can usually continue without again moving the large hand wheel, which is shown underneath the end of the shelf. As is readily understood, the operator propels the poises backward and forward by means of the hand wheel (at butt end of weighing beam) and cord passing around a pulley at the other end of the machine. By a little practice a person gets very expert, and can make a test with facility.

In the Olsen (Fig. 34), which is somewhat similar to the Riehlé machine, the stress is applied by means of a hand wheel and lever, so arranged that no torsional or transverse strain is imparted to the specimen, but a perfectly straight pull is secured.

The full capacity of the machine is registered by a poise moved on a single scale beam, by means of a cord and small hand wheel attached to the frame work of the machine, so the strain may be applied and weighed evenly and continuously throughout the test. It is also provided

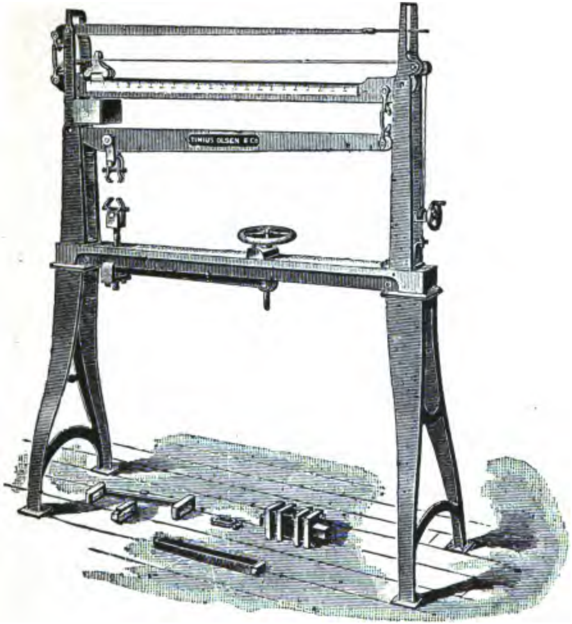

Fig. 35.

with grips resting on pivot bearings and so adjusted as to insure a perfectly straight pull on the specimen.

Whichever machine is used the load is to be applied at the rate of 400 pounds per minute.

None of these machines are free from sources of error. In the Michaelis and the Fairbanks machines there is an error due to the fact that some time (in which shot is falling into the bucket) is taken by the beam to fall to the valve checking the shot stream; even then there is a stream of shot extending from the valve opening to the surface of the shot in the bucket which must fall into the latter and be weighed as part of the load which broke the specimen, though this shot was not in the bucket when the specimen broke. In the other two forms mentioned, there is an error due to the fact that the chain is attached to the poise at a point not on a line with the knife edges of the beam, giving the poise a tendency to lift up or pull down.

Lack of Uniformity in Tensile Tests.

In cement testing, the personal equation enters very largely into the results. In a paper[1] by Prof. James Madison Porter, of Lafayette College, he gave a series of results upon the same cement by nine different operators, tested by the method of the Society of Civil Engineers as they understood it. The results varied from 75 to 247 pounds per square inch. The Committee on a Uniform System for Tests of Cement of the American Society of Civil Engineers, in their report, say:

"The testing of cement is not so simple a process as it is thought to be. No small degree of experience is necessary before one can manipulate the materials so as to obtain even approximately accurate results.

"The first test of inexperienced, though intelligent and careful persons, are usually very contradictory and inaccurate, and

---

[1] Engineering News, March 7, 1895.

no amount of experience can eliminate the variations introduced by the personal equations of the most conscientious observers. Many things, apparently of minor importance, exert such a marked influence upon the results, that it is only by the greatest care in every particular, aided by experience and intelligence that trustworthy tests can be made."

The personal equation probably plays its most important part in the gauging of the cement, the making of the mortar, and the molding and breaking of the briquettes. In order to eradicate these variations of treatment, machines have been introduced upon the market to do the work automatically and so do away with whatever variations the operator may introduce into the hand work, principally among which are the *jig* and the *Faija mixer*, and the *Bohme hammer*.

Jig Mixer.

The jig mixer in its simplest form consists of an ordinary "milk-shake" apparatus (see Fig. 4, page 46). After the proper proportions of water and cement have been ascertained, sufficient cement for one briquette is weighed into each cup and the desired amount of water poured upon it from a graduated cylinder. The covers are then fastened down upon the cups by means of thumb screws and the machine run for one minute, when the mortar is ready for the molds. In order that the briquettes made from mortar mixed in this machine shall be constant, it is necessary to give each lot of mortar the same number of revolutions in the same time. A description of the original and more complicated jig mixer may be found in a paper upon the St. Louis Water

Works Cement Testing Laboratory, by S. Bent Russell, C.E., in the *Engineering News*, 25, 2.

The Faija Mixer.

The Faija mixer is the design of the late Henry Faija, of England. Fig. 36 shows the mixer as made by Riehlé Bros. Testing Machine Co., of Philadelphia. It consists of a circular pan of about one foot in diameter, within which revolve the arms of a stirrer. These arms revolve around their own axis in one direction and around the pan in the reverse direction. This motion is given them by a fixed internally toothed wheel which actuates the pinion of the stirring spindle. To operate, first find by means of a trial test by hand gauging the proper proportion of water to cement. Next place in the mixer sufficient cement to fill a gang of molds and add at once the proper quantity of water for this weight of cement. Then turn the handle of the machine fairly quickly for from a half to three-quarters of a minute, when it will be found that the cement and water are thoroughly mixed and ready for the molds. In gauging cement and sand in this machine, first mix the cement and sand dry and then add the water, etc.

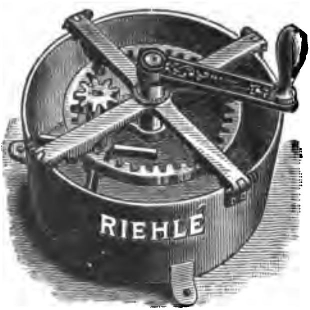

Fig. 36.

The Bohme hammer consists of a tilt hammer with automatic action. The hammer is thus described by Max

The Bohme Hammer.

Gary[1]: "The hammer is driven by a cam wheel of ten cams actuated by simple gearing. The wrought-iron handle of the hammer is let into the cross-head which carries the axle of the hammer and keyed to this cross-head and to the cap

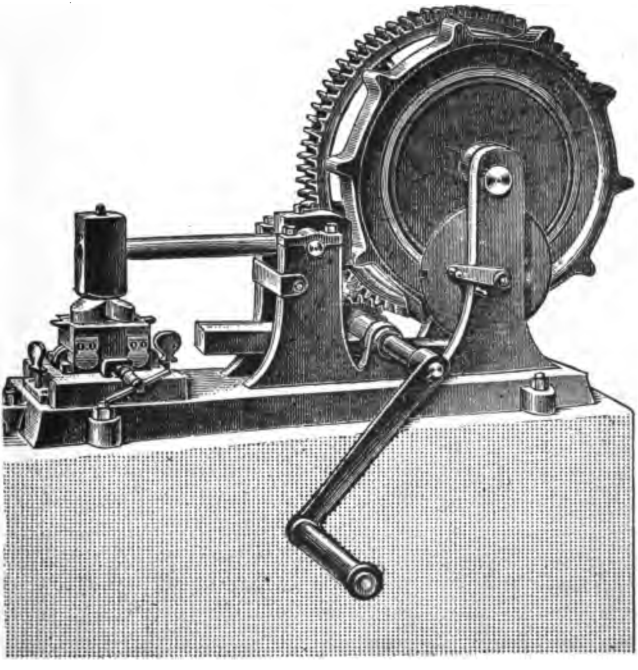

Fig. 37.

---

[1] Trans. Am. Soc. C.E., **30**, 1.

so that it may be replaced if worn. The steel hammer weighing 4½ pounds, is similarly fastened to the cap. As soon as the intended number of blows has been delivered, the mechanism is automatically checked, the proper setting having been made for this purpose before beginning the work." (The number of blows required in the German Standard test is 150.)

"The forms to receive the mortar consist of a lower and upper case held together by springs. The lower case for compression specimens consists of two angle irons held on a planed plate by a grinding strip and a screw acting on the latter. Upward motion is prevented by two wedge-shaped surfaces. The lower case and half the upper one is filled with the mortar to be tested and a plate laid upon its surface. On this plate the blows are delivered. It is of vital importance that the apparatus rests upon a firm non-elastic foundation; preferably it should be placed and fastened on a pier of masonry."

The Jameson Briquette Machine.

Prof. Charles D. Jameson describes, in his book on Portland cement, a form of machine in use in his laboratory at the University of Iowa. The main portion of the machine consists of a cylinder A (Figs. 38 and 39) which is flanged at the lower end, this flange corresponding in shape and size to the upper part of the base. The cylinder is bolted to the base by four bolts, each bolt provided with a filler that holds the lower face of the cylinder 1 inch above the base plate. Both of these faces are accurately planed. It is between these two planed faces that the molding plate swings, the fillers on the bolts acting as stops. The cylinder is made in two parts, bolted together. The bore is the size and shape of the briquette. In this bore works a solid plunger of the shape of the bore. The length of the plunger is sufficient to cover the feed hole when at its lowest point. The plunger is connected to the lever B by the connecting rod C. The molding plate swings in such a manner that when at either extreme, one of the openings is directly beneath the bore of the cylinder, while the other is directly over the extractor. These extractors are of the shape of the opening in the molding plate and are

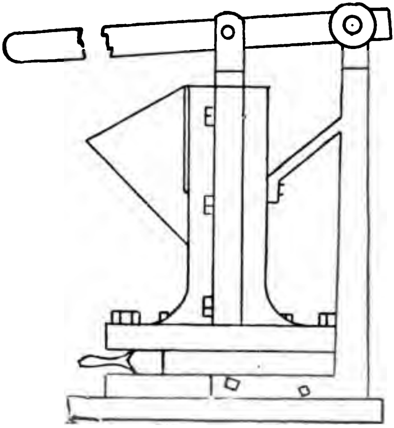

Fig. 38.

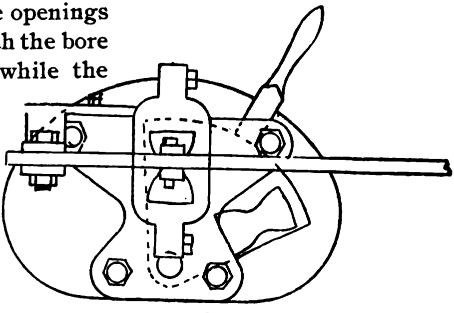

Fig. 39.

raised by levers. When the extractor is at its lowest point its top is a little below the lower side of the molding plate. The object of the extractors is to force the briquette from the mold. On the outside of the cylinder is the hopper.

The method of operation is as follows: The piston is raised until it is above the feed hole, and the cement or mortar in the hopper is forced into the cylinder. The molding plate is pushed against one of the stops so as to bring one of the openings under the cylinder bore. The lever is forced down causing the plunger to force the cement or mortar into the opening in the molding plate. The molding plate is then swung against the other stop. This movement cuts off the briquette and places it directly over the extractor. The other opening in the molding plate is directly under the cylinder bore. The extractor is raised by its lever, and the briquette forced out and removed. The extractor is lowered, the main plunger forced down again, the molding plate swung and another briquette made. The cylinder holds sufficient mortar for three briquettes. It should then be filled again. In the machine as described there is no way of regulating the amount of pressure. Experiments made by Prof. Jameson, however, indicate that there is no necessity of this, probably from the fact that the actual pressure is so great under all circumstances that the actual variation forms but a small percentage of it, not sufficient to vary the results.

To do away with the personal equation in the breaking of the briquette, Prof. J. M. Porter, professor of civil engineering in Lafayette College, has designed an ingenious form of cement-testing machine. In breaking a briquette with this machine, the attention of the operator is not required after the proper adjustment of the test-piece in the clips. He describes his machine as follows:[1]

Porter-Olsen Testing Machine.

The load is applied by water flowing into a tank suspended from the long arm of a very sensitive 15 to 1 lever. The weight of the lever and tank is counterbalanced by an adjustable weight on the left. Water is admitted to the tank from a large reservoir on the roof under a practically constant head of 90 feet, so there is no sensible variation of pressure in the stream admitted through a carefully fitted gate valve in the supply pipe. The position of this valve at "on," "off," and all intermediate points is shown by an index attached to the stem of the valve and registering on a dial marked off with the number of pounds per minute applied to the specimen as determined and verified by previous experiment.

When the briquettes break, the lever drops a few inches, then the plunger at the right end of the lever enters the pneumatic stop, and the lever and tank are gradually brought to rest. During the fall of the tank and before it comes to rest, a chain attached to the end of the valve stem in the tank is brought into tension and arrests the descent of the valve before its seat stops descending. The opening of this valve allows the contents of the tank to be quickly discharged into a hopper placed upon the floor, and is then carried off through a waste pipe to the sewer. As soon as the tank has discharged its contents, the weight on the left end of the lever brings the lever and tank into the position , the valve taking its seat during this movement and the machine is ready for another break. The actual

---

[1] Engineering News, March 7, 1895.

load can be applied at from 0 to 80 pounds per minute, thus giving an increase of stress of from 0 to 1,200 pounds per minute. The speed generally used is 400 pounds per minute, and with the valve set for this speed the needle beam will float every time within $\frac{1}{5}$ second of the proper time.

The stress on the specimen is measured by a poise traveling on a graduated scale beam, which can be read by means of a vernier to 1 pound and can be moved automatically or by hand at the wish of the operator. The automatic movement is accomplished by the following described device:

The horizontal disk and its engaged friction wheel are driven continuously by the pulley placed at the lower end of the vertical shaft and belted to overhead shafting. This friction wheel is feathered to a sleeve that runs loose on its shaft and carries a coned clutch that is nominally disengaged from its cone, which is also feathered to the shaft, and can be moved slightly longitudinally on the shaft into contact with the clutch by the action of the vertical lever.

When the needle beam rises, it makes contact through a vertical pin in the top of the frame, which completes an electric circuit and sends a current through the electro-magnet and causes it to attract its armature at the lower end of the vertical lever, which, moving to the right, engages the friction clutch and causes the shaft to revolve. This shaft operates the sprocket wheel and chain, which draw out the poise on the scale beam until the needle beam drops, breaking the electric circuit. Breaking the electric circuit releases the armature and allows the friction clutch to disengage and the poise comes to rest. The friction wheel may be set at a greater or less distance from the center of the disk by turning the capstan head nut, and the chain is overhauled faster or slower, causing the poise to move accordingly. If desired, the poise may be operated by the hand wheel without interfering with the automatic device other than cutting out the circuit. The chain is attached to the poise in line with the three knife-edges of the scale beam, hence the tension in the chain has no tendency to lift up or pull down the poise. This point is often overlooked in designing this detail, not only in cement machines, but in testing machines in general. The writer has a cement machine in which the error due to this cause is over 15 pounds.

SOUNDNESS

Importance of the Test.

The most important quality of cement is soundness, for no watter how high a degree of tensile strength a cement may develop at comparatively short periods, if it fails to resist the disintegrating influences of the atmosphere or the water in which it may be placed, it is useless as a material of construction. This tendency to disintegrate, fall to a powder, crack or expand on mixing the cement with water is termed "blowing." This fault is usually due to improper mixing of the raw materials allowing an excess of lime over what will combine with the silica and alumina of the cement mixture; or an improper burning failing to raise the temperature to the point where all the lime may combine with the silica and alumina, thus leaving some in the uncombined state. The free lime on coming in contact and combining with the water expands causing the cement to crack and fall to pieces.

The soundness of cement is generally tested by making small pats or cakes of neat cement gauged with water on glass plates. In size these pats are ½ inch thick at the middle, tapering to a thin edge, and are from 3 to 4 inches in diameter. These pats are placed in water and in air and watched carefully for signs of blowing such as cracks or distortion. The quantity of water used in gauging the cement is about the same as is required in preparing the mortar for tensile strength briquettes. Greater variations, however, will give more uniform results than would be allowable in tensile tests. The cakes should be kept moist during setting and until they are immersed to avoid drying cracks. The test as recommended by the Committee of the American Society of Civil Engineers is as follows:

Cold Test.

"Make two cakes of neat cement two or three inches in diameter, and about one-half inch thick, with thin edges. Note the time in minutes that these cakes when mixed with water to the consistency of stiff plastic mortar, take to set hard enough to stand the wire test recommended by General Gilmore, $^1/_2$-inch diameter wire loaded with $^1/_4$ of a pound, and $^1/_{24}$ inch loaded with 1 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 due to free lime, will disappear with age. The remaining cake should be kept in air and its color observed, which for a good cement should be uniform throughout, yellowish blotches indicating a poor quality, the Portland cements being of a bluish gray and the natural cements being dark or light according to the character of the rock of which they are made. The color of the cements when left in air indicates the quality much better than when they are put in water."

The rules of the Association of German Cement Manufacturers specify that the test shall be made as follows:

"In carrying out this test, the pat prepared for determining the time of set (see page 128) should be placed under water at the end of twenty-four hours, in the case of slow setting cements, but in any case only after it has become set. This may be done much quicker in the case of quick-setting cements. The pats, especially in the case of slow-setting cements, must be well protected from draughts, and the direct rays of the sun, until after they have become set. The best method is to place them in a closed box or cover them with damp cloths. Hair cracks which are caused by shrinkage, due to rapid drying, will thus be avoided. These generally appear in the center of the pat and are often mistaken by the uninitiated for cracks caused by blowing. If the cement shows any crumbling, or cracks are visible during the process of hardening while under water, this is a certain indication of the blowing of the cement; that is to say, the cement becomes cracked in consequence of an increase of volume and a gradual disruption of the particles previously connected takes place, which may ultimately lead to the total destruction of the mass. These symptoms of expansion usually appear within three days, but an observation extending over twenty-eight days is always sufficient."

In testing cement by the manner given above it is important that the testing should be continued over a long space of time. Many blowy, unsound cements will not show signs of cracks or distortion under twenty-eight days, some will not show it even at this date, yet in time the pats will fall to pieces and ultimately disintegrate. For this reason many methods have been proposed and tried for showing in a shorter time whether or not a cement is reliable and fit to use. In most of these methods the chemical action which causes the blowing or expanding, and which is extended sometimes over a considerable period of time, is hastened by the aid of heat as suggested by Michaelis or by the use of chemicals in preparing the mortar for the pats as suggested by Candlot, who used calcium chlorid.

Accelerated Tests.

Probably the best of the hot tests is that of the English cement expert, Henry Faija. His method consists in subjecting a freshly gauged pat upon a plate of glass prepared as directed above to a moist heat of 100° to 105° F. for six or seven hours, or until thoroughly set, and then immersing it in water kept at a temperature of 115° to 120° F. for the remainder of the twenty-four hours. This treatment imparts an artificial age to the cement and quickly brings out any vicious qualities the cement may possess. For this test he uses the apparatus shown in Fig. 40. It consists of a covered vessel in which water is kept at the even temperature of 115° to 120° F. by means of a water-jacket. The inner vessel is filled with water to the height shown. Above the water-

Faija's Test.

level is placed a rack. When the water in the inner vessel is at the temperature of 115° to 120° F. the upper part of the vessel will be filled with aqueous vapor and this latter will be at a temperature of from 100° to 105° F. As soon as the pat is gauged it is put on the rack and left there for six hours. It is then placed in the warm water and allowed to remain eighteen hours longer. The author of the test states that if a test pat after the above treatment shows no signs of cracking or blowing and adheres firmly to the glass plate on which it was made, it may be used with perfect confidence; it will never blow. This test certainly seems fairer to the cement than most of the hot tests, many of which would, if applied to some really good cements, cause them to be rejected.

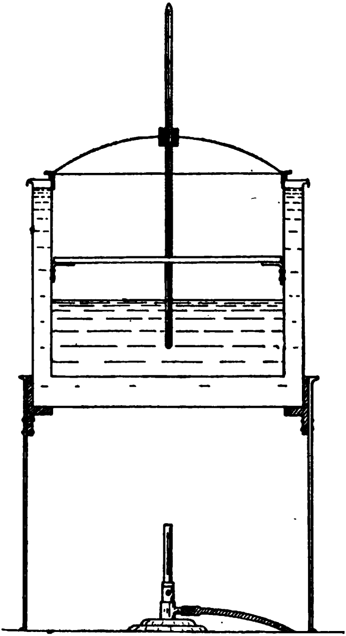
Fig. 40.

Captain W. W. Maclay modifies this test as follows: Four pats are prepared in the usual manner. One of these pats is placed in a steam-bath of a temperature of 195°

Maclay's Test.

to 200° F., as soon as made. The second pat is placed in the same bath as soon as it will bear the one pound wire. The third pat is placed in the steam-bath after double the interval has passed that took the second pat to set hard, counting from the time of gauging. The fourth pat is placed in the steam-bath after twenty-four hours. The four pats are kept in the steam-bath three hours, when they are immersed in water at 200° F. for twenty-one hours each, when they are taken out and examined. All four pats after being twenty-one hours in hot water, should, to pass the test perfectly, upon examination show no swelling, cracks, nor distortions, and should adhere to the glass plates. This latter requirement, while it obtains with some cements nearly free from uncombined lime, is not insisted upon, the cracking, swelling, and distortion being the more important features of the test. Where the cement is very objectionable from excess of free lime the trouble generally shows itself in the cracking or distortion of all four pats. Where the cement is not so bad, the cracking and swelling takes place on the first three pats only. With less objectionable cement only the first two pats crack or swell while the cracking and swelling of the first pat can generally be disregarded.

Captain Maclay does not consider this test final, however, but where the cement fails to pass gives it another chance by testing briquettes conserved in hot water and comparing with those kept in cold water. He found, in a general way, that the average tensile strength of hot water briquettes of pure cement four days old are nearly as high as the normal seven-day cold, while the hot water seven-day briquettes require nearly the same strain to pull them apart as the normal twenty-eight day cold, when the cement is of good quality. In a poor cement, however, one in which the pats show distortion and cracking, there is generally a marked falling off of the hot water briquettes from the above comparison, and one system can be used to check the other. The briquettes are prepared at the same time the regular cold water test-pieces are made—four additional sets of five each for neat cement and four additional sets of mortar. These are allowed to set twenty-one hours in moist air of about 60° F. They are placed three hours in the steam-bath at 195° F. and then immersed in hot water (200° F.), after which they are broken when two, three, four, and seven days old respectively, and the breakings compared with the normal breakings of briquettes seven and twenty-eight days old kept in cold water.

Kiln Test.

Dr. Bohme suggests the kiln test. The Association of German Cement Makers recommend this test as a means of quickly judging of the quality of a cement, but do not make the test decisive and abide by their twenty-eight-day test on these cements which fail to pass the kiln test. Their method for the test is as follows:

"For making the heat test, a stiff paste of neat cement and water is made, and from this cakes 8 cm. to 10 cm. in diameter and 1 cm. thick are formed on a smooth impermeable plate covered with blotting-paper. Two of these cakes which are to be protected against drying in order to prevent drying cracks, are placed after the lapse of twenty-four hours, or at least only after they have set, with their smooth surface on a metal plate and exposed for at least one hour to a temperature of from 110° C. to 120° C. until no more water escapes. For this purpose the drying closets in use in chemical laboratories[1] may be utilized. If after this treatment the cakes show no edge cracks, the cement is to be considered in general of constant volume. If such cracks do appear the cement is not to be condemned, but the results of the decisive test with the cakes hardening on glass plates under water must be waited for. It must, however, be noticed that the heat test does not admit of a final conclusion of the constancy of volume of those cements which contain more than 3 per cent. of calcium sulphate (gypsum) or other sulphur combinations."

Prof. Tetmajer, of Zurich, modifies this method by placing on the bottom of the oven a few millimeters of water. The heat is gradually applied so as to evaporate all the water in from three to six hours: first that on the floor of the oven, and then that absorbed by the mortar. The latter is held on a shelf above the floor. The temperature of the oven remains at about 95° C. until the water is entirely evaporated. After this the heating is continued half an hour longer in such a manner as to raise the temperature of the oven to 120° C. This will bring the temperature of the interior of the briquette at a little over 100° C. It is difficult to obtain comparative results

---

[1] See page 18.

by this method as the heat is not the same for all specimens, since after the evaporation of the water, the heat is much greater at the bottom than at the top of the oven.

Boiling Test.

This test, also devised by Prof. Tetmajer, is very similar to the one just given. It consists in rolling a ball of mortar and then flattening the ball to the thickness of half an inch. The consistency of the mortar should be such that it shall neither crack in flattening nor run at the edges. These pats are placed in a vessel of cold water immediately after gauging and heat applied and regulated so that the water boils in about an hour. The boiling is continued for three hours, when the pats are removed and examined for checking and cracking.

Calcium Chlorid Test.

Candlot discovered by a series of experiments upon cement that if the cement is either gauged with or kept in water containing calcium chlorid the free lime in it is slaked much more quickly. The more concentrated the solution the more marked the effect. The action of the salt is, therefore, similar to that of heat, to increase the chemical action causing expansion. If the cement is gauged with a concentrated solution of calcium chlorid, the lime will probably all be slaked before the cement sets, so that no cracking will occur on hardening, even if much free lime is present. If, however, the calcium chlorid solution is more dilute (40 grams to the liter) it will only cause slaking of a very small percentage of the free lime, such a small percentage as is unobjectionable in cements. If a pat made of this mortar is then kept in a calcium chlorid solution of the same strength, the slaking of the rest of the lime will be greatly hastened and cracking will soon appear if a harmful quantity of free lime is present. To carry out the test, gauge the cement with a 4 per cent solution (40 grams to the liter) of calcium chlorid, make into pats upon glass plates and allow to set, after which immerse the pats in the cold 4 per cent solution of calcium chlorid for twenty-four hours and then remove and examine for cracks, softening, etc.

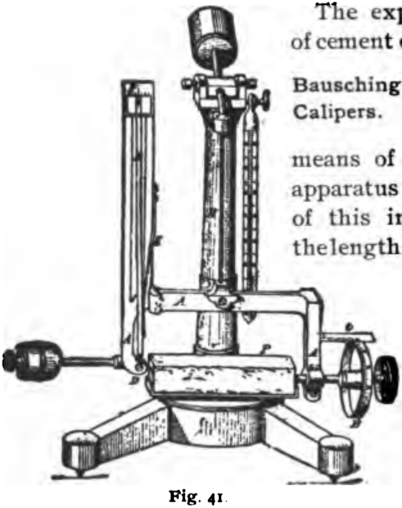
Fig. 41

Bauschinger's Calipers.

The expansion or contraction of cement during hardening may be measured directly and very accurately by means of Baushinger's caliper apparatus (Fig. 41). By means of this instrument changes in the length of small parallelopipedons, 100 mm. long and 5 sq. cm. cross section, may be accurately measured to within 1/200 mm. The apparatus consists of a stirrup-shaped caliper, having a fine micrometer screw on its right arm, the left being the support of a sensitive lever. The shorter arm of this lever terminates in a blunt caliper point and is pressed against the measuring screw by a spring attached to the long arm. The calipers are readily moved in any direction and the micrometer is read in the usual manner. One revolution of the screw equals 0.5 mm. and the readings on the head are made at 1/200 mm. The specimen is molded with square cavities in the end, and in these are set plates of glass containing centers for the caliper points. The molding is done similar to that for tension specimens except that both sides should be repeatedly struck off smooth. It requires but a few minutes to measure a specimen by this apparatus.

THE DETECTION OF ADULTERATION IN PORTLAND CEMENT

Cements are adulterated with hydraulic lime, blast-furnace slag, ground limestone, shale, ashes, etc. Some of these substances are so similar to Portland cement that chemical analysis fails to show their presence. It is, therefore, necessary to direct special tests to their detection. When present in small quantities, it is probable that even such tests will fail to show positively an adulterated cement.

Tests of Drs. R. and W. Fresenius.

Drs. R. and W. Fresenius,[1] at the request of the Association of German Cement Manufacturers, made investigations into the subject of cement adulteration looking to a method of detecting the same. They experimented upon twelve samples of pure Portland cement from Germany, England, and France, and compared the results of tests upon these with the results obtained by similar tests upon three kinds of hydraulic lime, three kinds of weathered slag, and two of ground slag. The cements were of various ages and had been exposed to the air for various lengths of time. Below are tabulated their experiments for comparison.

---

[1] Ztschr. anal. Chem., **23**, 175, and **24**, 66.

Description.	1 Specific gravity.	2 Loss on ignition. Per cent.	3 Alkalinity imparted to water by 0.5 gram. cc. of decinormal acid.	4 Volume of normal acid neutralized by 1 gram.	5 Weight of $KMnO_4$ reduced by 1 gram.	Weight of CO_2 absorbed by 3 grams.
				cc.	mg.	mg.
Portland cement A	3.155	1.58	6.25	20.71	0.79	1.4
" " B	3.125	2.59	4.62	21.50	2.38	1.6
" " C	3.155	2.11	4.50	20.28	0.93	1.8
" " D	3.144	1.98	5.10	21.67	1.12	1.0
" " E	3.144	1.25	6.12	19.60	0.98	1.6
" " F	3.134	2.04	4.95	20.72	1.21	1.1
" " G	3.144	0.71	4.30	22.20	0.89	0.0
" " H	3.125	1.11	4.29	20.30	1.07	0.7
" " J	3.134	1.00	4.00	19.40	2.01	0.0
" " K	3.144	0.34	4.21	20.70	0.98	0.0
" " L	3.154	1.49	4.60	18.80	2.80	0.3
" " M	3.125	1.25	5.50	20.70	2.33	0.0
Hydraulic lime A	2.441	18.26	20.23	21.35	1.40	27.8
" " B	2.551	17.82	22.73	26.80	0.93	31.3
" " C	2.520	19.60	19.72	19.96	0.98	47.7
Weathered slag A	3.012	0.76	0.91	14.19	74.60	3.6
" " B	3.003	1.92	0.70	13.67	60.67	3.5
" " C	2.967	1.11	1.00	9.70	44.34	2.9
Ground slag I	3.003	0.32	0.31	3.60	64.40	2.4
" " II	2.873	0.43	0.11	8.20	73.27	2.2

As the result of these experiments they proposed the following tests for the detection of adulteration:

Proposed Tests.

1. The specific gravity.

This must not be lower than 3.10.

2. The loss on ignition.

This should be between 0.3 and 2.59 per cent; certainly not much more.

3. The alkalinity imparted to water. 0.5 gram of cement should not render 50 cc. of water so alkaline as to require more than 6.25 cc. nor less than 4 cc. of decinormal acid to neutralize.

4. The volume of normal acid neutralized.

One gram of cement should neutralize from 18.8 to 21.7 cc. of normal acid.

5. The volume of potassium permanganate reduced.

One gram of cement should reduce not much more than 0.0028 gram of potassium permanganate.

6. The weight of carbon dioxid absorbed.

Three grams of cement should not absorb more than 0.0018 gram of carbon dioxid.

The tests 1, 3, 4, and 5 are for the detection of slag and 1, 2, 3, and 6 for the detection of hydraulic lime.

Drs. R. and W. Fresenius also tried these tests upon experimental mixtures containing 10 per cent of slag or hydraulic lime, and in each case were able to detect the impurity.

The methods employed for carrying out the tests were as follows:

Carrying Out the Tests.

1. They used for taking the specific gravity the method of Schuman (see page 123), with turpentine as the liquid. The end of the tube was corked to prevent evaporation, the temperature kept constant, and the vessel carefully shaken to displace air bubbles.

2. For loss on ignition 2 grams of cement were weighed into a tared crucible, and then heated over a Bunsen burner

for twenty minutes. The loss shown on again weighing was the loss on ignition.

3. For the "alkalinity to water test." The substance was finely powdered and passed through a sieve of 5,000 meshes to the square centimeter.[1] Of the resulting powder, 1 gram was shaken up with 100 cc. of distilled water without warming for ten minutes. The solution was then passed through a dry filter-paper into a dry vessel and 50 cc. of the filtrate titrated with decinormal hydrochloric acid.[2]

4. For "standard acid necessary to decompose." One gram of the fine powder obtained in 3 was shaken with 30 cc. of normal hydrochloric acid[3] and 70 cc. of water for ten minutes, without warming, and filtered through a dry filter-paper, 50 cc. of the filtrate were then titrated with normal caustic soda.[4]

5. For the volume of permanganate reduced. One gram of the fine powder, obtained in 3, was treated with a mix-

---

[1] 32,260 meshes to the square inch.

[2] To make decinormal hydrochloric acid, refer to page 84 with the notes under this section, and taking such a quantity of dilute hydrochloric acid as contains 3.65 grams of HCl, dilute this volume to 1 liter. Check its value by one of the methods given in the section referred to. The $^2/_5$ N nitric acid may be diluted to $^1/_{10}$ N strength and used in place of the $^1/_{10}$ N hydrochloric acid.

[3] Normal acid should contain 36.5 grams of HCl per liter.

[4] To prepare normal caustic soda, refer to page 87, and using the above normal acid as a standard proceed as directed there. The $^2/_5$ N solutions used in checking the per cent of lime in cement mixture (see page 83) may be used for this test. In this case shake up the cement with a mixture of 75 cc. of $^2/_5$ normal acid and 25 cc. of water, and titrate back with the $^2/_5$ normal alkali.

ture of 50 cc. of dilute sulfuric acid (sp. gr. 1.12) and 100 cc. of water. The resulting solution was then titrated with potassium permanganate solution.[1]

6. For carbon dioxid absorbed, about 3 grams of the fine powder obtained as in 3, were placed in a weighed tube and a stream of carbon dioxid allowed to pass over it. The sample was then dried in a desiccator over sulfuric acid (sp. gr. 1.84) and weighed. The increase in weight gave the amount of *carbon* dioxid absorbed, a small calcium chlorid drying tube was placed after the tube containing the cement to absorb any water evolved.

Le Chatelier's Test.

Le Chatelier has devised a very neat test for the adulteration in cement, depending upon the lower density of the adulterant than of the cement. His method consists in separating these lighter impurities from the cement by means of a heavy liquid, a mixture of methyl iodid and benzene, prepared of such strength that they float upon its surface while the pure Portland sinks to the bottom.

Preparation of the Heavy Liquid.

As the first step the methyl iodid solution must be prepared. This should be of density 2.95 according to Le Chatelier. As the density of the methyl iodid itself is 3.1, benzene must be added in small quantities until a crystal of aragonite (serving as a guide) whose density is 2.94 just remains at the surface. Since very small quan-

---

[1] Dissolve 0.28 gram of $KMnO_4$ in 100 cc. of water. Not much more than 1 cc. of this solution, or 2 cc. of the solution used to determine ferric oxid in cement (page 53) should be required if the cement is unadulterated.

tities of benzene change the density of the methyl iodid considerably it is well to make two solutions, one a little above and one a little below the density sought, and then to add the one to the other until the required density is obtained. By this means a more gradual change is affected and the danger of overrunning the mark is lessened.

Apparatus.

Le Chatelier used in his experiments a little glass tube 10 mm. in diameter and 70 mm. long. The tube (Fig. 42) is widened at the top to a funnel and drawn at the bottom with a regular slope to an opening of 1 mm. diameter. This opening is closed on the interior a little above the bottom by a plunger consisting of a small emery ground-glass stopper on the end of a glass rod, which projects above the funnel top.

Fig. 41

Test.

To make a test the stopper is wet with water to make a tight joint and inserted into the opening of the tube. Grease cannot be used as it is dissolved by the methyl iodid solution. Ten grams of the suspected cement are weighed into the tube and 5 cc. of methyl iodid solution (sp. gr. 2.95), prepared as above, poured upon it. A thin platinum wire bent into a loop around the plunger is then moved around and up and down in the liquid in a lively manner in order to drive out all air bubbles and mix the cement and liquid thoroughly. The apparatus is now set aside for an hour, when it will be found that the slag is on top and the cement below. The apparatus is now placed over a dry filter, the stopper raised and the cement and part of the liquid allowed to run out. The cement is retained upon the filter while the liquid is caught in a vessel below and may be used again. The slag and the rest of the liquid are then run out upon another filter, and the excess of liquid caught in a vessel for use again. The filters containing the slag and cement are washed with benzene, dried and weighed separately. From the weights the percentage of adulteration can be calculated. The slag and cement can then be analyzed chemically, if thought necessary, as a further guide.

Microscopic Test.

The microscope furnishes us with a very good means of detecting added material in cement. Butler[1] recommends that those particles which pass a 76 sieve and are retained upon a 120 sieve be examined with a low power (say a one-inch) objective. The particles of pure, well-burned cement clinker of this size will then appear dark, almost black in color, resembling coke somewhat, and will possess the characteristic spongy honey-combed appearance of cement clinker. The particles of less well-burned clinker, always present in cement, will, when examined in the same way, present the same shape and structure, but will differ in color, being light brown and semitransparent, resembling gum arabic. Intermediate products range from black to light brown. These particles are always of a more or less rounded nature. Particles of slag of the same size viewed under the same conditions differ somewhat in color, according to the nature of the slag. Usually the particles are light colored of angular fracture, and instead of the particles presenting

---

[1] "Portland Cement," p. 273.

a rounded appearance the edges are sharp like flint. Not to be mistaken for the slag, however, are the particles of débris from the millstones used to grind the clinker. These latter may be distinguished from the slag by picking out the particles in question with a pair of pincers, crushing them in a small agate mortar and treating them with hydrochloric acid. The slag is readily attacked while the débris from the millstones is not attacked. Particles of iron from the crusher are also present in the residue caught upon the 120 sieve. These may be identified by their black metallic appearance and their behavior with the magnet. Unburned coke is present when coal or coke has been used in burning the cement. This may be readily distinguished by its brilliant black color and by picking out the black particles with a pair of tweezers and heating on platinum foil, when the coke will, of course, burn to an ash.

APPENDIX

Tables

1. Table of the Atomic Weights of the More Important Elements. O = 1

Name.	Symbol	Weight	Name.	Symbol	Weight
Aluminum	Al	27.1	Iron	Fe	56.0
Antimony	Sb	120.4	Lead	Pb	206.9
Arsenic	As	75.0	Magnesium	Mg	24.1
Barium	Ba	137.4	Manganese	Mn	55.0
Bismuth	Bi	208.1	Mercury	Hg	200.0
Boron	B	11.0	Nickel	Ni	58.7
Bromine	Br	80.0	Nitrogen	N	14.0
Cadmium	Cd	112.4	Oxygen	O	16.0
Calcium	Ca	40.1	Phosphorus	P	31.0
Carbon	C	12.0	Platinum	P	194.9
Chlorin	Cl	35.5	Potassium	K	39.11
Chromium	Cr	52.1	Silicon	Si	28.4
Cobalt	Co	59.0	Silver	Ag	107.9
Copper	Cu	63.6	Sodium	Na	23.1
Fluorin	F	19.1	Strontium	Sr	87.6
Gold	Au	197.2	Sulfur	S	32.1
Hydrogen	H	1.0	Tin	Sn	119.1
Iodin	I	126.9	Zinc	Zn	65.4

TABLE OF FACTORS

Found.	**Sought.**	**Factor.**	**Found.**	**Sought.**	**Factor.**
CdS	CaS	0.50000	$Mg_2P_2O_7$	MgO	0.36190
$CaSO_4$	CaO	0.41185	$Mg_2P_2O_7$	$MgCO_3$	0.75722
$CaSO_4$	$CaCO_3$	0.73504	K_2PtCl_6	K_2O	0.19398
CaS	$CaSO_4$	1.8872	K_2PtCl_6	KCl	0.30701
CO_2	C	0.27272	$NaCl$	Na_2O	0.53076
CO_2	$CaCO_3$	2.2743	$BaSO_4$	S	0.13734
CO_2	$MgCO_3$	1.9154	$BaSO_4$	SO_3	0.34291
$AgCl$	HCl	0.25424	$BaSO_4$	H_2SO_4	0.42006
Fe	Fe_2O_3	1.4284	$BaSO_4$	$CaSO_4$	0.58565
Fe_2O_3	Fe	0.70007	$BaSO_4$	CaS	0.30895

TABLE FOR CONVERTING $CaSO_4$ TO CaO.

	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.00	0.0000	0.0041	0.0082	0.0124	0.0165	0.0206	0.0247	0.0288	0.0329	0.0371
0.10	0.0412	0.0453	0.0494	0.0536	0.0577	0.0618	0.0659	0.0700	0.0741	0.0783
0.20	0.0824	0.0865	0.0906	0.0947	0.0988	0.1030	0.1071	0.1112	0.1153	0.1194
0.30	0.1236	0.1277	0.1318	0.1359	0.1400	0.1441	0.1483	0.1524	0.1583	0.1606
0.40	0.1647	0.1688	0.1730	0.1771	0.1812	0.1853	0.1894	0.1936	0.1977	0.2018
0.50	0.2059	0.2100	0.2142	0.2183	0.2224	0.2265	0.2306	0.2348	0.2389	0.2430
0.60	0.2471	0.2512	0.2553	0.2595	0.2636	0.2677	0.2718	0.2759	0.2801	0.2842
0.70	0.2883	0.2924	0.2965	0.3007	0.3048	0.3089	0.3130	0.3171	0.3212	0.3254
0.80	0.3295	0.3336	0.3377	0.3418	0.3460	0.3501	0.3542	0.3583	0.3624	0.3665
0.90	0.3707	0.3748	0.3789	0.3830	0.3871	0.3913	0.3954	0.3995	0.4036	0.4077
1.00	0.4119	0.4160	0.4201	0.4242	0.4283	0.4324	0.4366	0.4407	0.4448	0.4489
1.10	0.4530	0.4572	0.4613	0.4654	0.4695	0.4736	0.4777	0.4819	0.4860	0.4901
1.20	0.4942	0.4983	0.5025	0.5066	0.5107	0.5148	0.5189	0.5230	0.5272	0.5313
1.30	0.5354	0.5395	0.5436	0.5478	0.5519	0.5560	0.5601	0.5642	0.5683	0.5725
1.40	0.5766	0.5807	0.5848	0.5889	0.5931	0.5972	0.6013	0.6054	0.6095	0.6137
1.50	0.6178	0.6219	0.6260	0.6301	0.6342	0.6384	0.6425	0.6466	0.6507	0.6548
1.60	0.6590	0.6631	0.6672	0.6713	0.6754	0.6795	0.6837	0.6878	0.6919	0.6960
1.70	0.7001	0.7043	0.7084	0.7125	0.7166	0.7207	0.7249	0.7290	0.7331	0.7372

Example to explain the use of the above table—To convert 1.5261 grams of $CaSO_4$ to CaO.

From line 1.50 column 0.02, 1.52 grams $CaSO_4$ = 0.6260 gram CaO.
From line 0.60 column 0.01, 0.0061 gram $CaSO_4$ = 0.002512 gram CaO.

1.5261 grams $CaSO_4$ = 0.628512 gram CaO.

TABLE FOR CONVERTING $Mg_2P_2O_7$ TO MgO.

	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.00	0.0000	0.0036	0.0072	0.0109	0.0145	0.0181	0.0217	0.0253	0.0290	0.0326
0.10	0.0362	0.0398	0.0434	0.0470	0.0507	0.0543	0.0579	0.0615	0.0652	0.0688
0.20	0.0724	0.0760	0.0796	0.0832	0.0868	0.0905	0.0941	0.0977	0.1013	0.1049
0.30	0.1086	0.1122	0.1158	0.1194	0.1230	0.1267	0.1303	0.1339	0.1375	0.1411
0.40	0.1448	0.1484	0.1520	0.1556	0.1592	0.1629	0.1665	0.1701	0.1737	0.1773
0.50	0.1810	0.1846	0.1882	0.1918	0.1954	0.1991	0.2027	0.2063	0.2099	0.2135
0.60	0.2171	0.2208	0.2244	0.2280	0.2316	0.2352	0.2389	0.2425	0.2461	0.2497
0.70	0.2533	0.2569	0.2606	0.2647	0.2678	0.2714	0.2750	0.2787	0.2873	0.2859
0.80	0.2895	0.2931	0.2968	0.3004	0.3040	0.3076	0.3112	0.3149	0.3185	0.3221
0.90	0.3257	0.3293	0.3330	0.3366	0.3402	0.3438	0.3474	0.3511	0.3547	0.3583
1.00	0.3619	0.3655	0.3691	0.3728	0.3764	0.3800	0.3836	0.3872	0.3909	0.3945

Example: To convert 0.0828 gram of $Mg_2P_2O_7$ to MgO.

From line 0.80, column 0.02, 0.082 gram $Mg_2P_2O_7$ = 0.02968 gram MgO.

From line 0.00, column 0.08, 0.0008 gram $Mg_2P_2O_7$ = 0.00029 gram MgO.

0.0828 gram $Mg_2P_2O_7$ = 0.02997 gram MgO.

SPECIFIC GRAVITIES OF NITRIC ACID.

Specific gravities at $\frac{15^\circ}{4^\circ}$ C.	Degrees Baumé.	Degrees Twaddell	100 parts by weight contain		1 liter contains kilograms of		Correction of sp. gr. for ± 1° C.
			N_2O_5.	HNO_3	N_2O_5.	HNO_3.	
1.00	0	0	0.08	0.10	0.001	0.001	0.0001
1.01	1.4	2	1.62	1.90	0.016	0.019	0.0001
1.02	2.7	4	3.17	3.70	0.033	0.038	0.0001
1.03	4.1	6	4.71	5.50	0.049	0.057	0.0002
1.04	5.4	8	6.22	7.26	0.064	0.075	0.0002
1.05	6.7	10	7.71	8.99	0.081	0.094	0.0002
1.06	8.0	12	9.15	10.68	0.097	0.113	0.0003
1.07	9.4	14	10.57	12.33	0.113	0.132	0.0003
1.08	10.6	16	11.96	13.95	0.129	0.151	0.0004
1.09	11.9	18	13.31	15.53	0.145	0.169	0.0004
1.10	13.0	20	14.67	17.11	0.161	0.188	0.0004
1.11	14.2	22	16.00	18.67	0.177	0.207	0.0005
1.12	15.4	24	17.34	20.23	0.195	0.227	0.0005
1.13	16.5	26	18.66	21.77	0.211	0.246	0.0005
1.14	17.7	28	19.98	23.31	0.228	0.266	0.0006
1.15	18.8	30	21.29	24.84	0.245	0.286	0.0006
1.16	19.8	32	22.60	26.36	0.262	0.306	0.0006
1.17	20.9	34	23.90	27.88	0.279	0.326	0.0007
1.18	22.0	36	25.18	29.38	0.297	0.347	0.0007
1.19	23.0	38	26.47	30.88	0.315	0.367	0.0007
1.20	24.0	40	27.74	32.36	0.333	0.388	0.0007
1.21	25.0	42	28.99	33.82	0.351	0.409	0.0008
1.22	26.0	44	30.24	35.28	0.369	0.430	0.0008
1.23	26.9	46	31.53	36.78	0.387	0.452	0.0008
1.24	27.9	48	32.82	38.29	0.407	0.475	0.0008
1.25	28.8	50	34.13	39.82	0.427	0.498	0.0009
1.26	29.7	52	35.44	41.34	0.447	0.521	0.0009
1.27	30.6	54	36.75	42.87	0.467	0.544	0.0009
1.28	31.5	56	38.07	44.41	0.487	0.568	0.0009
1.29	32.4	58	39.39	45.95	0.508	0.593	0.0010
1.30	33.3	60	40.71	47.49	0.529	0.617	0.0010
1.31	34.2	62	42.06	49.07	0.551	0.643	0.0010
1.32	35.0	64	43.47	50.71	0.573	0.669	0.0011
1.33	35.8	66	44.89	52.37	0.597	0.697	0.0011
1.34	36.6	68	46.35	54.07	0.621	0.725	0.0011
1.35	37.4	70	47.82	55.79	0.645	0.753	0.0011
1.36	38.2	72	49.35	57.57	0.671	0.783	0.0012
1.37	39.0	74	50.91	59.39	0.698	0.814	0.0013
1.38	39.8	76	52.52	61.27	0.725	0.846	0.0013
1.39	40.5	78	54.20	63.23	0.753	0.879	0.0013
1.40	41.2	80	55.97	65.30	0.783	0.914	0.0013
1.41	42.0	82	57.86	67.50	0.816	0.952	0.0014
1.42	42.7	84	59.83	69.80	0.849	0.991	0.0014
1.43	43.4	86	61.86	72.17	0.885	1.032	0.0014
1.44	44.1	88	64.01	74.68	0.921	1.075	0.0015
1.45	44.8	90	66.24	77.28	0.961	1.121	0.0015
1.46	45.4	92	68.56	79.98	1.001	1.168	0.0015
1.47	46.1	94	71.06	82.90	1.045	1.219	0.0015
1.48	46.8	96	73.76	86.05	1.092	1.274	0.0015
1.49	47.4	98	76.80	89.60	1.144	1.335	0.0015
1.50	48.1	100	80.65	94.09	1.210	1.411	0.0016
1.51	48.7	102	84.09	98.10	1.270	1.481	0.0017
1.52	49.4	104	85.44	99.67	1.299	1.515	0.0017

INDEX

pse nel