QUARRY PRODUCTS OF IOWA

6

S. W. BEYER IRA A. WILLIAMS

·

. .

BY

S. W. Beyer and Ira A. Williams

• Ŷ -

and the second sec

BY S. W. BEYER AND IRA A. WILLIAMS

_

CONTENTS

,

P	age
The materials and manufacture of Portland cement	33
Introduction	33
Complex cements	33
Classes of silicate cements	34
Pozzuolanic cements	34
Hydraulic limes	34
Natural cements	34
Portland cements	34
Natural cements	35
Portland cement	37
Puzzolan cement	37
Portland cement	38
Definition	38
Composition and constitution	40
Raw materials for Portland cement	41
General considerations	41
Raw material actually in use	43
Argillaceous limestone	43
Pure hard limestone	44
Soft limestone, chalk	44
Fresh water marls	45
Alkali waste	46
Blast-furnace slag	47
Clays and shales	48
Slate	49
Factors determining the value of deposits of cement materials	50
Methods and cost of excavation of the raw materials	50
Quarrying	50
Mining.	51
Dredging	52
Cost of raw materials at the mill	52
Methods of manufacture	54
Preparation of the mixture for the kiln	55

ŕ

Drying the raw materials	55
Percentage of water in raw materials	55
Methods and costs of drying	57
Grinding and mixing	58
Dry methods	58
Wet methods	59
Composition of the mixture	62
Burning the mixture	63
Summary of burning process	64
Theoretical fuel requirements	64
Losses of heat in practice	65
Actual fuel requirements and output	66
Effect of composition on burning	66
Character of kiln coal	67
Drying coal	67
Pulverizing coal	68
Total cost of coal preparation	68
Clinker grinding	69
Addition of Gypsum	70
Constitution of Portland cement	71
Testing of raw materials to determine availability for manufacture of Portland	
cement	73
Methods of testing	76
Analysis of limestones	76
Process of analysis	76
Treatment of siliceous residue	78
Analysis of clays	79
Interpretation of analyses	82
Determination of hydraulic factor	83
Calculation of cement mixtures	85

32

CHAPTER I

THE MATERIALS AND MANUFACTURE OF PORTLAND CEMENT.

The following general treatise on the properties of the raw materials and the processes of manufacture of Portland cement is taken largely from the report of Mr. E. C. Eckel, on Cement Materials of Iowa, Iowa Geological Survey, Volume XV. According to Eckel's grouping, the so-called Complex Cements only, are considered in this chapter. In order to indicate the relation existing between Portland and other complex cementing materials, a brief presentation is given of the characteristics of the more commonly used silicate cements.

COMPLEX CEMENTS.

The cementing materials grouped here as Silicate or Hydraulic Cements include all those materials whose setting properties are due to the formation of new compounds, during manufacture or use, and not to the mere reassumption of the original composition of the material from which the cement was made. These new compounds may be formed either by chemical change during manufacture or by chemical interaction, in use, of materials which have merely been mechanically mixed during manufacture.

In the class of silicate cements are included all the materials commonly known as cements by the engineer (natural cements, Portland cement, pozzuolanic cements), together with the hydraulic limes.

Though differing widely in raw material, methods of manufacture and properties, the silicate cements agree in two prominent features; they are all hydraulic (though in very different

degree); and this property of hydraulicity is, in all, due largely or entirely to the formation of tri-calcic silicate $(3CaO.SiO_2)$. Other silicates of lime as well as silico-aluminates, may also be formed; but they are relatively unimportant, except in certain of the natural cements and hydraulic limes where the lime-aluminates may be of greater importance than is here indicated. This will be recurred to in discussing the groups named.

The silicate cements are divisible, on technologic grounds, into four distinct classes. The basis for this division is given below. It will be seen that the first named of these classes (the pozzuolanic cements) differs from the other three very markedly, inasmuch as its raw materials are not calcined after mixture; while in the last three classes the raw materials are invariably calcined after mixture. The four classes differ somewhat in composition but more markedly in methods of manufacture and in the properties of the finished cements.

CLASSES OF SILICATE CEMENTS.

1. *Pozzuolanic or Puzzolan Cements;* produced by the mechanical mixture, without calcination, of slaked lime and a silicoaluminous material (the latter being usually a volcanic ash or blast-furnace slag).

2. *Hydraulic Limes*: produced by the calcination, at a temperature not much higher than that of decarbonation, of a siliceous limestone so high in lime carbonate that a considerable amount of free lime appears in the finished product. See Chapter II.

3. Natural Cements; produced by the calcination, at a temperature between those of decarbonation and clinkering, of a siliceous limestone (which may also carry notable amounts of alumina and of magnesium carbonate) in which the lime carbonate is so low, relative to the silica and alumina, that little or no free lime appears in the cement.

4. Portland Cements; produced by the calcination, at the temperature of semi-vitrefaction ("clinkering") of an artificial mixture of calcareous with silico-aluminous materials, in the proportion of about three parts of lime carbonate to one part of clayey material.

NATURAL CEMENTS.

Natural cements are produced by burning a naturally impure limestone, containing from fifteen to forty per cent of silica, alumina, and iron oxide. This burning takes place at a comparatively low temperature, about that of ordinary lime burning. The operation can therefore be carried on in a kiln closely resembling an ordinary lime kiln. During the burning the carbon dioxide of the limestone is almost entirely driven off, and the lime combines with the silica, alumina and iron oxide, forming a mass containing silicates, aluminates, and ferrites of lime. In case the original limestone contained much magnesium carbonate, the burned rock will also contain a corresponding amount of magnesia.

After burning, the burned mass will not slake if water be added. It is necessary, therefore, to grind it quite finely. After grinding, if the resulting powder (natural cement) be mixed with water it will harden rapidly. This hardening or setting will also take place under water. The natural cements differ from ordinary limes in two noticeable ways:

(1) The burned mass does not slake on the addition of water.

(2) After grinding, the powder has hydraulic properties, i. e., if properly prepared, it will set under water.

Natural cements are quite closely related to both hydraulic lines on the one hand, and Portland cement on the other, agreeing with both in the possession of hydraulic properties. They differ from hydraulic lines, however, in that the burned natural cement rock will not slake when water is poured on it.

The natural cements differ from Portland cements in the following important particulars:

(1) Natural cements are not made by burning carefully prepared and finely ground artificial mixtures, but by burning masses of natural rock.

(2) Natural cements, after burning and grinding, are usually yellow to brown in color and light in weight, their specific gravity being about 2.7 to 2.9; while Portland cement is commonly blue to gray in color and heavier, its specific gravity ranging from 3.0 to 3.2.

(3) Natural cements are always burned at a lower temperature than Portland, and commonly at a *much* lower temperature, the mass of rock in the kiln never being heated high enough to even approach the fusing or clinkering point.

(4) In use, natural cements set more rapidly than Portland cement, but do not attain such a high ultimate strength.

(5) In composition, while Portland cement is a definite product whose percentages of lime, silica, alumina and iron oxide vary only between narrow limits, various brands of natural cements will show very great differences in composition.

The material utilized for natural cement manufacture is invariably a clayey linestone, carrying from 13 to 35 per cent of clayev material, of which 10 to 22 per cent or so is silica, while alumina and iron oxide together may vary from 4 to 16 per cent. It is the presence of these clayey materials which gives the resulting cement its hydraulic properties. Stress is often carelessly or ignorantly laid on the fact that many of our best known natural cements carry large percentages of magnesia, but it should, at this date, be realized that magnesia (in natural cements at least) may be regarded as being almost exactly interchangeable with lime, so far as the hydraulic properties of the product are concerned. The presence of magnesium carbonate in a natural cement rock is then merely incidental, while the silica, alumina, and iron oxide are essential. The thirty per cent or so of magnesium carbonate which occurs in the cement rock of the Rosendale district, N. Y., could be replaced by an equal amount of lime carbonate, and the burnt stone would still give a hydraulic product. If, however, the clayey portion (silica, alumina, and iron oxide) of the Rosendale rock could be removed, leaving only the magnesium and lime carbonates, the burnt rock would lose all of its hydraulic properties and would vield simply a magnesian lime.

This point has been emphasized because many writers on the subject have either explicitly stated or implied that it is the magnesium carbonate of the Rosendale, Akron, Louisville, Utica and Milwaukee rocks that causes them to yield a natural cement on burning.

PORTLAND CEMENT.

Portland cement is produced by burning a finely ground, artificial mixture containing essentially lime, silica, alumina, and iron oxide, in certain definite proportions. Usually this combination is made by mixing limestone or marl with clay or shale, in which case about three times as much of the lime carbonate should be present in the mixture as of the clay materials. The burning takes place at a high temperature, approaching 3,000° F., and must therefore be carried on in kilns of special design and lining. During the burning, combination of the lime with silica, alumina, and iron oxide takes place. The product of the burning is a semi-fused mass called clinker, and consists of silicates, aluminates and ferrites of lime in certain definite proportions. This clinker must be finely ground. After such grinding the powder (Portland cement) will set under water.

As noted above, under the head of Natural Cements, Portland cement is blue to gray in color, with a specific gravity of 3.0 to 3.2, and sets more slowly than natural cements, but soon attains a higher tensile strength.

PUZZOLAN CEMENTS.

The cementing materials included under this name are made by mixing powdered slaked lime with either a volcanic ash or a blast-furnace slag. The product is therefore simply a mechanical mixture of two ingredients, as the mixture is not burned at any stage of the process. After mixing, the mixture is finely ground. The resulting powder (Puzzolan cement) will set under water.

Puzzolan cements are usually light bluish in color, and of lower specific gravity and less tensile strength than Portland cement. They are better adapted to use under water than to use in air.

PORTLAND CEMENT.

DEFINITION.

In the following section various possible raw materials for Portland cement manufacture will be taken up, and their relative suitability for such use will be discussed. In order that the statements there made may be clearly understood it will be necessary to preface this discussion by a brief explanation regarding the composition and constitution of Portland cement.

Use of term Portland.—While there is a general agreement of opinion as to what is understood by the term Portland cement, a few points of importance are still open questions. The definitions of the term given in specifications are in consequence often vague and unsatisfactory.

It is agreed that the cement mixture must consist essentially of lime, silica and alumina in proportions which can vary but slightly; and that this mixture must be burned at a temperature which will give a semi-fused product—a "clinker." These points must therefore be included in any satisfactory definition. The point regarding which there is a difference of opinion is whether or not cements made by burning a natural rock can be considered true Portlands. The question as to whether the definition of Portland cement should be drawn so as to include or exclude such products is evidently largely a matter of convention; but, unlike most conventional issues, the decision has very important practical consequences. The question at issue may be stated as follows:

If we make artificial mixture of the raw materials and a very high degree of burning the criteria on which to base our definition, we must in consequence of that decision exclude from the class of Portland cements certain well known products manufactured at several points in France and Belgium, by burning a natural rock, without artificial mixture, and at a considerably

DEFINITION

lower temperature than is attained in ordinary Portland cement practice. These "natural Portlands" of France and Belgium have always been considered Portland cements by the most critical authorities, though all agree that they are not particularly *high grade* Portlands. So that a definition, based upon the criteria above named, will of necessity exclude from our class of Portland cements some very meritorious products.

There is no doubt that in theory a rock could occur, containing lime, silica and alumina in such correct proportions as to give a good Portland cement on burning. Actually, however, such a perfect cement rock is of extremely rare occurrence. As above stated, certain brands of French and Belgian "Portland" cements are made from such natural rocks, without the addition of any other material; but these brands are not particularly high grade, and in the better Belgian cements the composition is corrected by the addition of other materials to the cement rock, before burning.

The following definition of Portland cement is of importance because of the large amount of cement which will be accepted annually under the specifications^{*} in which it occurs. It is also of interest as being the nearest approach to an official government definition of the material that we have in this country.

"By a Portland cement is meant the product obtained from the heating or calcining up to incipient fusion of intimate mixtures, either natural or artificial, of argillaceous with calcareous substances, the calcined product to contain at least 1.7 times as much of lime, by weight, as of the materials which give the lime its hydraulic properties, and to be finely pulverized after said calcination, and thereafter additions or substitutions for the purpose only of regulating certain properties of technical importance to be allowable to not exceeding 2 per cent of the calcined product."

It will be noted that this definition does not require pulverizing or artificial mixing of the materials prior to burning. It seems probable that the Belgian "natural Portlands" were kept in mind when these requirements were omitted. In dealing with American made cements, however, and the specifications in question are headed, "Specifications for American Portland cement," it is a serious error to omit these requirements. No true Portland cements are at present manufactured in America from natural mixtures, without pulverizing and artificially mix-

39

^{*} Professional paper No. 28, Corps of Engineers, U. S. A., p. 30.

ing the materials prior to burning. Several plants, however, have placed on the market so-called Portland cements made by grinding up together the underburned and overburned materials formed during the burning of natural cements. Several of these brands contain from 5 to 15 per cent of magnesia, and under no circumstances can they be considered true Portland cements.

In view of the conditions above noted, the writer believes that the following definition will be found more satisfactory than the one above quoted.

Definition of Portland Cement.—Portland cement is an artificial product obtained by finely pulverizing the clinker produced by burning to semi-fusion an intimate mixture of finely ground calcareous and argillaceous material, this mixture consisting approximately of one part of silica and alumina to three parts of carbonate of lime (or an equivalent amount of lime oxide).

COMPOSITION AND CONSTITUTION.

Portland cements may be said to tend toward a composition approximating to pure tri-calcic silicate $(3\text{CaO}, \text{SiO}_2)$ which would correspond to the proportion CaO 73.6 per cent, SiO₂ 26.4 per cent. As can be seen, however, from the analyses quoted later, actual Portland cements as at present made differ in composition somewhat markedly from this. Alumina is always present in considerable quantity, forming with part of the lime, the dicalcic aluminate (2CaO. Al₂O₃). This would give, as stated by Newberry, for the general formula of a pure Portland—

$x(3CaO. SiO_2) + y(2CaO. Al_3O_3).$

But the composition is still further complicated by the presence of accidental impurities, or intentionally added ingredients. These last may be simply adulterants, or they may be added to serve some useful purpose. Calcium sulphate is a type of the latter class. It serves to retard the set of the cement, and, in small quantities, appears to have no injurious effect which would prohibit its use for this purpose. In dome kilns, sufficient sulphur trioxide is generally taken up by the cement from the fuel gases to obviate the necessity for the later addition of calcium sulphate, but in the rotary kiln its addition to the ground cement, in the form of either powdered gypsum or plaster of Paris, is a necessity.

Iron oxide, within reasonable limits, seems to act as a substitute for alumina, and the two may be calculated together. Magnesium carbonate is rarely entirely absent from limestone or clays, and magnesia is therefore almost invariably present in the finished cement. Though magnesia, when magnesium carbonate is burned at low temperature, is an active hydraulic material, it does not combine with silica or alumina at the clinkering heat employed in Portland cement manufacture. At the best it is an inert and valueless constituent in the cement; many regard it as positively detrimental in even small amounts, and because of this feeling manufcturers prefer to carry it as low as possible. Newberry has stated that in amounts of less than three and onehalf per cent it is harmless, and American Portlands from the Lehigh district usually reach well up toward that limit. In European practice it is carried somewhat lower.

Raw Materials.

GENERAL CONSIDERATIONS.

For the purpose of the present chapter it will be sufficiently accurate to consider that a Portland cement mixture, when ready for burning, will consist of about seventy-five per cent of lime carbonate (CaCO₃) and twenty per cent of silica (SiO₂), alumina (Al₂O₃) and iron oxide (Fe₂O₃) together, the remaining five per cent including any magnesium carbonate, sulphur and alkalies that may be present.

The essential elements which enter into this mixture, lime, silica, alumina and iron, are all abundantly and widely distributed in nature, occurring in different forms in many kinds of rocks. It can therefore readily be seen that, theoretically, a satisfactory Portland cement mixture could be prepared by combining, in an almost infinite number of ways and proportions, many possible raw materials. Obviously, too, we might expect to find perfect gradations in the artificialness of the mixture, varying from one extreme where a natural rock of absolutely correct composition was used to the other extreme where two or more materials, in nearly equal amounts, are required to make a mixture of correct composition.

The almost infinite number of raw materials which are theoretically available are, however, reduced to a very few in practice under existing commercial conditions. The necessity for making the mixture as cheaply as possible rules out of consideration a large number of materials which would be considered available if chemical composition was the only thing to be taken into account. Some materials otherwise suitable are too scarce; some are too difficult to pulverize. In consequence, a comparatively few combinations of raw material are actually used in practice.

In certain localities deposits of argillaceous (clayey) limestone or "cement rock" occur, in which the lime, silica, alumina and iron oxide exist in so nearly the proper proportions that only a relatively small amount (about ten per cent or so) of other material is required in order to make a mixture of correct composition.

In the majority of plants, however, most or all of the necessary lime is furnished by one raw material, while the silica, alumina and iron oxide are largely or entirely derived from another raw material. The raw material which furnishes the lime is usually natural, a limestone, chalk or marl, but occasionally an artificial product is used, such as the chemically precipitated lime carbonate which results as waste from alkali manufacture. The silica, alumina and iron oxide of the mixture are usually derived from clays, shales or slates; but in a few plants blast-furnace slag is used as the silico-aluminous ingredient in the manufacture of true Portland cement.

The various combinations of raw materials which are at present used in the United States in the manufacture of Portland cement may be grouped under six heads. This grouping is as follows:

- 1. Argillaceous limestone (cement rock) and pure limestone.
- 2. Pure hard limestone and clay or shale.
- 3. Soft chalky limestone and clay.
- 4. Marl and clay.
- 5. Alkali waste and clay.
- 6. Slag and limestone.

Raw Materials Actually in Use.

ARGILLACEOUS LIMESTONE: CEMENT ROCK.

An argillaceous limestone containing approximately 75 per cent of lime carbonate and 20 per cent of clayey materials (silica, alumina and iron oxide) would, of course, be the ideal material for use in the manufacture of Portland cement, as such a rock would contain within itself in the proper proportions all the ingredients necessary for the manufacture of a good Portland. It would require the addition of no other material, but when burnt alone would give a good cement. This ideal cement material is, of course, never realized in practice, but certain deposits of argillaceous limestone approach the ideal composition very closely.

The most important of these argillaceous limestone or "cement rock" deposits is, at present, that which is so extensively utilized in Portland cement manufacture in the "Lehigh district" of Pennsylvania and New Jersey. This area still furnishes about two-thirds of all the Portland cement manufactured in the United States.

The analyses given in the following table are fairly representative of the materials employed in the Lehigh district. The first four analyses are of "cement rock"; the last two are of the purer limestone used for mixing with it.

Silica (SiO_2)		Cemen	Limestone			
	$\begin{array}{c} 10.02\\ 6.26 \end{array}$	$9.52 \\ 4.72$	$14.52 \\ 6.52$	$\begin{smallmatrix}16.10\\2.20\end{smallmatrix}$	$3.02 \\ 1.90$	$1.98 \\ 0.70$
Iron oxide (Fe_2O_3) Lime carbonate $(CaCO_3)$ Magnesium carbonate $(MgCO_3)$	$ \begin{array}{c} 78.65 \\ 4.71 \end{array} $		$\begin{array}{c} \dots \\ 73.52\\ 4.69\end{array}$	$\begin{array}{c} \dots \\ 76.23 \\ 3.54 \end{array}$	$92.05 \\ 3.04$	$ \begin{array}{c} 95.19 \\ 2.03 \end{array} $

Analyses of Lehigh district cement materials.

"CEMENT ROCK" IN OTHER PARTS OF THE UNITED STATES.

Certain Portland cement plants, particularly in the western United States, are using combinations of materials closely similar to those in the Lehigh district. Analyses of the materials used at several of these plants are given in the following table:

	Utah		California		Colorado	
	Cemen trock	Limestone	Cement rock	Limestone	Cementrock	Limestone
Silica (SiO_2) Alumina (Al_2O_3) Iron oxide (Fe_2O_3) Lime carbonate $(CaCO_3)$	$21.2 \\ 8.0 \\ \\ 62.08$	6.8 3.0 89.8	20.06 10.07 3.39 63.40	$7.12 \\ 2.36 \\ 1.16 \\ 87.70$	$14.20 \\ 5.21 \\ 1.73 \\ 75.10$	88.0

Analyses of "cement rock" and limestone from the western United States.

PURE HARD LIMESTONES.

A series of analyses of representative pure hard limestones, together with analyses of the clays or shales with which they are mixed, is given below:

	Limestones				Clays a	and sha	les	
Silica (SiO_2)	1.72 1.63	0.86	0.56 1.23)	0.40	63.56	55.80	56.30	60.00
Iron oxide (Fe_2O_3)	6.59	1.03	0.29	0.44	27.32	30.20	29.86	4.32
Lime carbonate $(CaCO_3)$ Magnesium carbonate $(MgCO_3)$	90.58	97.06	$97.23 \\ 0.75$	$97.99 \\ 0.42$	$3.60 \\ 2.60$	2.54		1.70 1.50

Analyses of pure hard limestones and clayey materials.

The first limestone analysis given in the above table represents a curious type, used in several plants in the Middle West. As will be noted, it is a relatively impure limestone, but its principal impurity is iron oxide. It contains 8.22 per cent of iron oxide and alumina, as compared with 1.72 per cent of silica; and therefore demands great care in the selection of a suitable highsilica clay to mix with it.

SOFT LIMESTONE: CHALK. ORIGIN AND GENERAL CHARACTER.

Chalk, properly speaking, is a pure carbonate of lime, composed of the remains of the shells of minute organisms, among which those of foraminifera are especially prominent. The

FRESH WATER MARLS.

chalks and soft limestones discussed here agree, not only in having usually originated in this way, but also in being rather soft and therefore readily and cheaply crushed and pulverized. As Portland cement materials they are, therefore, almost ideal. One defect, however, which to a small extent counterbalances their obvious advantages is the fact that most of these soft, chalky limestones absorb water quite readily. A chalky limestone which in a dry season will not carry over two per cent of moisture as quarried, may in consequence of prolonged wet weather show as high as fifteen or twenty per cent of water. This difficulty can of course be avoided if care be taken in quarrying to avoid unnecessary exposure to water and, if necessary, to provide facilities for storing a supply of the raw materials during wet seasons.

COMPOSITION.

In composition these chalks, or "rotten limestones," vary from a rather pure calcium carbonate, low in both magnesia and clayey materials to an impure clayey limestone, requiring little additional clay to make it fit for use in Portland cement manufacture. Analyses quoted from various authors of a number of these chalky limestones are given in the table below, and will serve to show their range of composition.

	Demopolis, Ala.	San Antonio, Tex.	Dallas, Tex.	White Cliffs, Ark,	Yankton, S. Dak.	Milton, N. Dak.
Silica (SiO_2)	12.13	5.77	23.55	7.97	8.20	9.15
Iron oxide (Fe_2O_3)	$\frac{3.17}{3.28}$	2.14	1.50	1.09	7.07	2.30
Lime carbonate $(CaCO_3)$ Magnesium carbon, $(MgCO_2)$	75.07	90.15	70.21	88.64	83.59 n. d.	63.75 1.25

Analyses of chalky limestones.

FRESH WATER MARLS.

Marls, in the sense in which the term is used in the Portland cement industry, are incoherent limestones which have been deposited in the basins of existing or extinct lakes. So far as

45-

chemical composition is concerned, marls are practically pure limestones, being composed almost entirely of calcium carbonate. Physically, however, they differ greatly from the compact rocks which are commonly described as limestones, for the marls are granular, incoherent deposits. This curious physical character of marls is due to the conditions under which they have been deposited, and varies somewhat according to the particular conditions which governed their deposition in different localities.

COMPOSITION.

As shown by the analyses below, marls are usually very pure lime carbonates. They therefore require the addition of considerable clay to bring them up to the proper composition for a Portland cement mixture.

The marls are readily excavated, but necessarily carry a large percentage of water. The mixture, on this account, is commonly made in the wet way, which necessitates driving off a high percentage of water in the kilns. Analyses of typical marls and clays are given in the following tables:

	Marl				Clay	
Silica (SiO_2) Alumina Al_2O_3) Iron oxide (Fe_2O_3)	$\left. \begin{array}{c} 0.25\\ .10 \end{array} \right\}$	3.0	$1.60 \\ 1.55$	40.48 20.95	52.0 { 17.0 { 5.0	$63.75 \\ 16.40 \\ 6.35$
Lime carbonate $(CaCO_3)$ Magnesium carbon. $(MgCO_3)$	94.39 .38	93.0 1.5	88.9 .94	25.80 .99	20.0	$\begin{array}{c} 4.0 \\ 2.1 \end{array}$

Analyses of marls and clays used in cement plants.

ALKALI WASTE.

A very large amount of waste material results from the process used at alkali works in the manufacture of caustic soda. This waste material is largely a precipitated form of calcium carbonate, and if it is sufficiently free from impurities, it furnishes a cheap source of lime for use in Portland cement manufacture.

The availability of alkali waste for this purpose depends largely on what process was used at the alkali plant. Leblanc process waste, for example, carries a very large percentage of sulphides, which prevents its use as a Portland cement material. Waste resulting from the use of the ammonia process, on the other hand, is usually a very pure mass of lime, mostly in the form of carbonate, though a little lime hydrate is commonly present. As pyrite is not used in the ammonia process, its waste is usually low enough in sulphur to be used as a cement material. The waste may carry a low or a very high percentage of magnesia, according to the character of the limestone that has been used in the alkali plant. When a limestone low in magnesium carbonate has been used, the resulting waste is a very satisfactory Portland cement material.

The following analyses are fairly representative of the waste obtained at alkali plants using the ammonia process:

Silica (SiO_2) 0.60 1.75 1.98 0.98 Alumina (Al_2O_3) 3.04 0.61 1.41 1.62 Iron oxide (Fe_2O_3) 53.33 50.60 48.29 50.40 Magnesia (MgO) 0.48 5.35 1.51 4.97 Alkalies (Na_2O, K_2O) 0.20 0.64 0.64 0.56 Sulphur trioxide (SO_3) n. d. n. d. 1.26 n. d. Sulphur (S) 0.00 1.42 60.90 0.98		1	2	3	
41.001 41.70 33.00 1.00	Silica (SiO_2) . Alumina (Al_2O_3) . Iron oxide (Fe_2O_3) . Lime (CaO) Magnesia (MgO) . Alkalies (Na_2O, K_2O) . Sulphur trioxide (SO_3) . Sulphur (S) . Carbon dioxide (CO_2) .	0.60 3.04 53.33 0.48 0.20 n. d. n. d. 42.43	1.75 0.61 50.60 5.35 0.64 n. d. 0.10 { 41 70	1.98 1.41 1.38 48.29 1.51 0.64 1.26 n. d. 39.60	0.98 1.62 50.40 4.97 0.50 n. d. 0.06 n. d.

Analyses of alkali waste.

Of the analyses quoted in the preceding table, those in the first and third columns represent materials which are actually used in Portland cement manufacture in England and the United States. The alkali wastes whose analyses are given in the second and fourth columns are notably too high in magnesia to be advisable for such use.

BLAST FURNACE SLAG.

True Portland cements, which must be sharply distinguished from slag (or puzzolan) cements, can be made from mixtures which contain blast furnace slag as one ingredient. In this case the slag is intimately mixed with limestone and the mixture is finely powdered. It is then burned in kilns and the resulting clinker pulverized.

The slags from iron furnaces consist essentially of lime (CaO), silica (SiO_2) and alumina $(Al_2 O_3)$, though small percentages of iron oxide (FeO), magnesia (MgO) and sulphur (S), are commonly present. Slag may, therefore, be regarded as a very impure limestone or a very calcareous clay, from which the carbon dioxide has been driven off. Two plants in the United States are at present engaged in the manufacture of true Portland cement from slag.

The slag used at a German Portland cement plant has the following range in composition:

Composition of slag used in Portland cement manufacture	•	
Silica (SiO ₂)	$_{\mathrm{to}}$	35.
Alumina (Al_2O_3) 10.	"	14.
Iron Oxide (FeO) 0.2	"	1.2
Lime (CaO)46.	" "	49.
Magnesia (MgO) 0.5	"	3.5
Sulphur trioxide (SO ₃) 0.2	" "	0.6

CLAYS AND SHALES.

Clays are ultimately derived from the decay of older rocks, the finer particles resulting from this decay being carried off and deposited by streams along their channels, in lakes, or along parts of the sea coast or sea bottom as beds of clay. In chemical composition the clays are composed essentially of silica and alumina, though iron oxide is almost invariably present in more or less amount, while lime, magnesia, alkalies and sulphur are of frequent occurrence, though usually in small percentages.

Shales are clays which have become hardened by pressure. The so-called "fire clays" of the coal measures are usually shales, as are many of the other "clays" of commerce.

For use as Portland cement materials clays or shales should be as free as possible from gravel and sand, as the silica present as pebbles or grit is practically inert in the kiln unless ground more finely than is economically practicable. In composition they should not carry less than 55 per cent of silica, and preferably from 60 to 70 per cent. The alumina and iron oxide together should not amount to more than one-half the percentage of silica, and the composition will usually be better the nearer the ratio

 $Al_2O_3 + Fe_2O_3 = \frac{SiO_2}{3}$ is approached.

SLATE.

Nodules of lime carbonate, gypsum or pyrite, if present in any quantity, are undesirable; though the lime carbonate is not absolutely injurious. Magnesia and alkalies should be low, preferably not above three per cent.

SLATE.

Slate is, so far as origin is concerned, merely a form of shale in which a fine, even and parallel cleavage has been developed by pressure. In composition, therefore, it will vary exactly as do the shales, and so far as composition alone is concerned, slate would not be worthy of more attention, as a Portland cement material, than any other shale.

Commercial considerations in connection with the slate industry, however, make slate a very important possible source of cement material. Good roofing slate is a relatively scarce material, and commands a good price when found. In the preparation: of roofing slate for the market so much material is lost during sawing, splitting, etc., that only about ten to twenty-five per cent of the amount quarried is salable as slate. The remaining seventy-five to ninety per cent is of no service to the slate miner. It is sent to the dump heap and is a continual source of trouble and expense. This very material, however, as can be seen from the analyses quoted below, is often admirable for use, in connection with limestone, in a Portland cement mixture. As it is a waste product, it could be obtained very cheaply by the cement manufacturer.

	Maximum	Average	Minimum				
Silica (SiO ₂)	68.62	60.64	54.05				
Alumina $(\tilde{\Lambda}l_2O_3)$	24.71	18.05	9.77				
Iron oxides (FeO, Fe ₂ O ₃)	10.66	6.87	2.18				
Lime (CaO)	5.23	1.54					
Magnesia (MgO)	6.43	2.60	0.12				
Alkalies $(\dot{K}_2 O, \dot{N} a_2 O)$	8.68	4.74	1.93				
Ferrous sulphide (FeS _*)		0.38					
Carbon dioxide (CO ₂)		1.47					
Water of combination		3.51					
Moisture, below 110°C	b	0.62					

4

Composition of American roofing states.

49'

Factors Determining the Value of Deposits of Cement Materials.

It seems desirable to give a somewhat detailed discussion of the factors which influence the value of limestone, marl or chalk or clay for Portland cement manufacture. Determining the possible value, for Portland cement manufacture, of a deposit of raw material is a complex problem, since the value depends upon a number of distinct factors, all of which must be given due consideration. The more important of these factors are:

(1) Chemical composition of the material.

(2) Physical character of the material.

(3) Amount of material available.

(4) Location of the deposit with respect to transportation routes.

(5) Location of the deposit with respect to fuel supplies.

(6) Location of the deposit with respect to markets.

METHODS AND COST OF EXCAVATION OF RAW MATERIALS.

The natural raw materials used at present in Portland cement manufacture are obtained by one of three methods,—(a) quarrying, (b) mining, and (c) dredging. When the cement manufacturer is given an opportunity to choose between these different methods of excavation, his choice will depend partly on the physical character of the material to be excavated and partly on the topographic and geologic conditions. Usually, however, there is no opportunity for a choice of methods, for in any given case one of the methods will be so evidently the only possible mode of handling the material as to leave no room for other considerations.

The three different methods of excavation will first be briefly considered, after which the cost of raw materials at the mill will be discussed.

Quarrying.—In the following pages the term "quarrying" will be used to cover all methods of obtaining raw materials from open excavations—quarries, cuts or pits—whether the material excavated be a limestone, a shale or a clay. Quarrying is the most natural and common method of excavating the raw materials for cement manufacture. If marl, which is usually worked by dredging, be excluded from consideration, it is probably within safe limits to say that 95 per cent of the raw materials used at American Portland cement plants are obtained by quarrying. If marks be included, the percentages excavated by the different methods would probably be about as follows: Quarrying, 88 per cent; dredging, 10 per cent; mining, 2 per cent.

In the majority of limestone quarries the material is blasted out and loaded by hand on cars or carts. In a few limestone quarries a steam shovel is employed to do the loading, and in shale quarries this use of the steam shovel is more frequent. In certain clay and shale pits, where the materials are of suitable character, the steam shovel does all the work, both excavating and loading the raw materials.

The rock is usually shipped to the mill as quarried without any treatment except sledging it to a convenient size for loading. At a few quarries, however, a crushing plant is installed at the quarry, and the rock is sent as crushed stone to the mill. A few plants also have installed their driers at the quarry, and dry the stone before shipping it to the mill. Except the saving of mill space thus attained, this practice seems to have little to commend it.

Mining.—The term "mining" will be used, in distinction from "quarrying," to cover methods of obtaining any kind of raw material by underground workings, through shafts or tunnels. Mining is, of course, rarely employed in excavating materials of such low value per ton as the raw materials for Portland cement manufacture. Occasionally, however, when a thin bed of limestone or shale is being worked, its dip will carry it under such a thickness of other strata as to make mining cheaper than stripping and quarrying, for that particular case.

Mining is considerably more expensive work than quarrying but there are a few advantages about it that serve to counterbalance the greater cost per ton of raw material. A mine can be worked steadily and economically in all kinds of weather, while an open cut or quarry is commonly in a more or less unworkable condition for about three months of the year. Material won by mining is, moreover, always dry and clean.

Dredging.—The term "dredging" will be here used to cover all methods of excavating soft, wet, raw materials. The fact that the materials are wet implies that the deposit occurs in a basin or depression; and this in turn, implies that the mill is probably located at a higher elevation than the deposit of raw material, thus necessitating up-hill transportation to the mill.

The only raw material for Portland cement manufacture that is extensively worked by dredging, in the United States, is marl. Occasionally the clay used is obtained from deposits overlain by more or less water; but this is rarely done except where the marl and clay are interbedded or associated in the same deposit.

A marl deposit, in addition to containing much water diffused throughout its mass, is usually covered by a more or less considerable depth of water. This will frequently require the partial draining of the basin in order to get tracks laid near enough to be of service.

In dredging marl the excavator is frequently mounted on a barge, which floats in a channel resulting from previous excavation. Occasionally, in deposits which either were originally covered by very little water or have been drained, the shovel is mounted on a car, running on tracks laid along the edge of the deposit.

The material brought up by the dredge may be transported to the mill in two different ways, the choice depending largely upon the manufacturing processes in use at the plant. At plants using dome or chamber kilns, or where the marl is to be dried before sending to the kiln, the excavated marl is usually loaded by the shovel on cars, and hauled to the mill by horse or steam power. At normal marl plants, using a very wet mixture, it is probable that the second method of transportation is more economical. This consists of dumping the marl from the excavator into tanks, adding sufficient water to make it flow readily, and pumping the fluid mixture to the mill in pipes.

COST OF RAW MATERIALS AT MILL.

The most natural way, perhaps, to express the cost of the raw materials delivered at the mill would be to state it as being so many cents per ton or cubic yard of raw material, and this is the method followed by quarrymen or miners in general. To the cement manufacturer, however, such an estimate is not so suitable as one based on the cost of raw materials per ton or barrel of finished cement.

In the case of hard and comparatively dry limestones or shales, it may be considered that the raw material loses 331_{\odot} per cent in weight on burning. Converting this relation into pounds of raw material and of clinker we find that 600 pounds of dry raw material will make about four hundred pounds of clinker. Allowing something for other losses in the process of manufacture, it is convenient and sufficiently accurate to estimate that 600 pounds of dry raw material will give one barrel of finished cement. These estimates must be increased if the raw materials carry any appreciable amount of water. Clays will frequently contain 15 per cent or more of water, while soft chalky limestones, if quarried during wet weather, may carry as high as 15 to more than 20 per cent. A Portland cement mixture composed of a pure chalky limestone and a clay might, therefore, average 10 to 20 per cent of water, and consequently about seven hundred pounds of such a mixture would be required to make one barrel of finished cement.

With marls the loss on drying and burning is much greater. Russell states^{*} that according to determinations made by E. D. Campbell, one cubic foot of marl, as it usually occurs in the normal deposits, contains about forty-seven and one-half pounds of line carbonate and forty-eight pounds of water. In making cement from a mixture of marl and clay, therefore, it would be necessary to figure on excavating and transporting more than one thousand pounds of raw material for every barrel of finished cement.

From the preceding notes it will be understood that the cost of raw materials at the mill, per barrel of cement, will vary not only with the cost of excavation but with the kind of materials in use.

In dealing with hard, dry materials, extracted from open quarries near the mills, the cost of mining raw materials may vary between eight cents and fifteen cents per barrel of cement. The lower figure named is probably about the lowest attainable with

^{*22}d Ann. Rept. U. S. Geol. Surv., pt. 3, p. 657.

good management and under favorable natural conditions; the higher figure is probably a maximum for fairly careful management of a difficult quarry under eastern labor conditions. When it is necessary to mine the materials, the cost will be somewhat increased. Cement rock has been mined at a cost equivalent to ten cents per barrel of cement, but this figure is attained under particularly favorable conditions. The cost of mining and transportation may reach from this figure up to twenty cents per barrel.

With regard to wet marks and clays, it is difficult to give even an approximate estimate. It seems probable, however, when the dead weight handled is allowed for, that these soft materials will cost almost as much, delivered at the mill, per barrel of finished cement, as the hard dry limestones and shales.

Methods of Manufacture.

If, as in the present discussion, we exclude from consideration the so-called "natural Portlands," Portland cement may be regarded as being an artificial product, obtained by burning to semi-fusion an intimate mixture of pulverized materials, this mixture containing lime, silica and alumina, varying in proportion only within certain narrow limits; and by crushing finely the clinker resulting from this burning.

If this restricted definition of Portland cement be accepted, four points may be regarded as being of cardinal importance in its manufacture. These are:

(1) The cement mixture must be of the proper chemical composition.

(2) The materials of which it is composed must be carefully ground and intimately mixed before burning.

(3) The mixture must be burned at the proper temperature.

(4) After burning, the resulting clinker must be finely ground.

The first named of these points, the chemical composition of the mixture, can be more advantageously discussed after the other three points have been disposed of. The subjects will therefore be taken up in the following order:

Preparation of the mixture for the kiln.

Burning the mixture.

Grinding the clinker, addition of gypsum, etc. Composition and properties of Portland cement.

PREPARATION OF THE MIXTURE FOR THE KILN.

The preparation of the mixture for the kiln involves the reduction of both of the raw materials to a very fine powder, and their intimate mixture. In practice the raw materials are usually crushed more or less finely, and then mixed, after which the final reduction to powder takes place. Two general methods of treatment, the dry and the wet, are in use at different plants. Unless the limy constituent of the mixture is a marl, already full of water, the dry method is almost invariably followed. This consists merely in keeping the materials in as dry a condition as possible throughout the entire process of crushing and mixing; and, if the raw materials originally contained a little moisture, they are dried before being powdered and mixed. In the wet method, on the other hand, the materials are powdered and mixed while in a very fluid state, containing sixty per cent or more of water.

Drying the raw materials.—With the exception of the marls and clays used in the wet method of manufacture, Portland cement materials are usually dried before grinding is commenced. This is necessary because the raw materials, as they come from the quarry, pit or mine, will almost invariably carry appreciable, though often very small, percentages of water, which greatly reduces the efficiency of most modern types of grinding mills, and tends to clog the discharge screens.

Percentage of water in raw materials.—The percentage of water thus carried by the crude raw material will depend largely on the character of the material; partly on the method of handling and storing it; and partly on weather conditions.

In the case of hard limestones, freshly quarried, the water will commonly range from $\frac{1}{2}$ to 3 per cent, rarely reaching or exceeding the higher figure except in the very wet quarries or during the rainy season. Such limestones, comparatively dry when quarried, are frequently sent to the grinding mills without artificial drying.

55

With the soft, chalky limestones, which absorb water very rapidly, the percentage can usually be kept down to 5 per cent or less in dry weather; while prolonged wet weather may necessitate the handling at the mill of material carrying as high as 15 to 20 per cent of water.

The clays present a much more complicated case. In addition to the hygroscopic or mechanically-held water that they may contain, there is also always present a certain percentage of chemically combined water. The amount of hygroscopic water present will depend on the treatment and exposure of the clay; and may vary from 1 per cent or so in clays which have been stored and air dried to as high as 30 per cent in fresh clays. The chemically combined water will depend largely on the composition of the clay, and may vary from 5 to 12 per cent. The hygroscopic or mechanically-held water of clays can be driven off at a temperature of 212° F., while the chemically combined water is lost only at a low red heat. The total water, therefore, to be driven off from clays may range from 6 to 42 per cent, depending on the weather, the drainage of the clay pit, and the care taken in preventing unnecessary exposure to moisture of the excavated clay. The average total amount of moisture will probably be about 15 per cent.

In dealing with shales, the mechanically-held water will rarely rise above 10 per cent, and can commonly be kept well below that limit. An additional 2 to 7 per cent of water will be carried by any shale, in a state of chemical combination.

At a few plants marl is used, with clay, in a dry process. As noted elsewhere the marls, as excavated, carry usually about 50 per cent of water. This case presents a more difficult problem than do the other raw materials, because the vegetable matter usually present in marls is extremely retentive of water.

It will be seen, therefore, that coment materials may carry from one per cent to fifty per cent of water when they reach the mill. In a dry process it is necessary to remove practically all of this water before commencing the grinding of the materials. One reason for this is that fine pulverizing can not be economically or satisfactorily accomplished unless absolutely dry material is fed to the grinding machinery. Another reason, which is

PREPARATION OF THE MIXTURE FOR THE KILN.

one of convenience rather than of necessity, is that the presence of water in the raw materials complicates the calculation of the cement mixture.

Methods and costs of drying.—The type of dryer commonly used in cement plants is a cylinder approximately five feet in diameter and forty feet or so in length, set at a slight inclination to the horizontal and rotating on bearings. The wet raw material is fed in at the upper end of the cylinder, and it moves gradually toward the lower end, under the influence of gravity, as the cylinder revolves. In many dryers angle irons are bolted to the interior in such a way as to lift and drop the raw material alternately, thus exposing it more completely to the action of the heated gases, and materially assisting in the drying process. The dried raw material falls from the lower end of the cylinder into an elevator boot, and is then carried to the grinding mills.

The drying cylinder is heated either by a separate furnace or by waste gases from the cement kilns. In either case the products of combustion are introduced into the cylinder at its lower end, are drawn through it, and escape up a stack set at the upper end of the dryer.

The dryer above described is the simplest, and is most commonly used. For handling the small percentages of water contained in most cement materials it is very efficient, but for dealing with high percentages of water, such as are encountered when marl is to be used in a dry process, it seems probable that double heating dryers will be found more economical. This type is exemplified by the Ruggles-Coles dryer. In this dryer a double cylinder is employed. The wet raw material is fed into the space between the inner and outer cylinders, while the heated gases pass first through the inner cylinder, and then, in a reverse direction, through the space between the inner and outer cylinders. This double heating type of dryer is employed in almost all of the slag cement plants in the United States, and is also in use in several Portland cement plants.

When vertical kilns were in use, drying floors and drying tunnels were extensively used, but at present they can be found in only a few plants, being everywhere else supplanted by the rotary dryers.

The cost of drying will depend on the cost of fuel, the percentage of water in the wet material and the type of dryer. Even under the most unfavorable conditions five pounds of water can be expected to be evaporated per pound of coal used, while a good dryer will usually evaporate seven or eight pounds of water per pound of coal.

GRINDING AND MIXING; DRY METHODS.

Part, at least, of the grinding is usually accomplished before the drying, but for convenience the subjects have been separated in the present paper. Usually the limestone is sent through a crusher at the quarry or mill before being dried, and occasionally the raw material is further reduced in a Williams mill, etc., before drying, but the principal part of the reduction always takes place after the material has been dried.

After the two raw materials have been separately dried they may be mixed immediately, or each may be further reduced separately before mixing. Automatic mixers, of which many types are on the market, give a mixture in proportions determined upon from analysis of the materials.

The further reduction of the mixture is usually carried on in two stages, the material being ground to about thirty mesh in a ball mill, komminuter, Griffin mill, etc., and finally reduced in a tube mill. At a few plants, however, single stage reduction is practiced in Griffin or Huntington mills, while at the Edison plant at Stewartsville, New Jersey, the reduction is accomplished in a series of rollers.

The majority of plants use either the Griffin mill and tube mill or the ball and tube mills, and there is probably little difference in the cost of operating these two combinations. The ball mill has never been quite as much of a success as its companion, the tube mill, and has been replaced at several plants by the komminuter.

Fineness of mixture.—After its final reduction, and when ready for burning, the mixture will usually run from 90 to 95 per cent through a 100-mesh sieve. In the plants of the Lehigh district the mixture is rarely crushed as fine as when limestone and clay are used. Newberry* has pointed out in explanation

^{*}Twentieth Ann. Rept. U. S. Geol. Surv., pt. 6, p.545.

for this that an argillaceous limestone (cement rock) mixed with a comparatively small quantity of purer limestone, as in the Lehigh plants, requires less thorough mixing and less fine grinding than when a mixture of limestone and clay (or marl and clay) is used, for even the coarser particles of argillaceous limestone will vary so little in chemical composition from the proper mixture as to affect the quality of the resulting cement but little, should either mixing or grinding be incompletely accomplished.

A very good example of typical Lehigh Valley grinding of raw material is afforded by a specimen^{*} examined by Prof. E. D. Campbell. This sample of raw mixture ready for burning was furnished by one of the best of the eastern Peunsylvania cement plants. A mechanical analysis of it showed the following results:

	М	esh of Sie	ve
	50	100	200
Per cent passing Per cent residue	$\begin{array}{c} 96.9\\ 3.1 \end{array}$	$\frac{85.6}{14.4}$	$72.4 \\ 27.6$

The material, therefore, is so coarsely ground that only a trifle over 85 per cent passes a 100-mesh sieve.

WET METHODS.

Wet methods of preparing Portland cement mixtures date back to the time when millstones and similar crude grinding contrivances were in use. With such imperfect machinery it was impossible to grind dry materials fine enough to give a good Portland cement mixture. The advent of good grinding machinery has practically driven out the wet methods of manufacture in this country, except in dealing with materials such as marls, which naturally carry a large percentage of water. One or two plants in the United States do, it is true, deliberately add water to a limestone-clay mixture; but the effect of this practice on the cost sheets of these remarkable plants is not encouraging.

In preparing cement mixtures from marl and clay, a few plants dry both materials before mixing. It seems probable that this practice will spread, for the wet method of mixture is inherently

^{*}Jour. Amer. Chem. Soc., vol. 25, p. 1106.

expensive. At present, however, almost all marl plants use wet methods of mixing, and it is therefore necessary to give some space to a discussion of such methods.

Certain points regarding the location, physical condition, and chemical composition of the marls and clays used in such mixtures have important effects upon the cost of the wet process. As regards location, considered on a large scale, it must be borne in mind that marl deposits of workable size occur only in the Northern States and in Canada. In consequence the climate is unfavorable to continuous working throughout the year, for the marl is usually covered with water, and in winter it is difficult to secure the material. In a minor sense location is still an important factor, for marl deposits necessarily and invariably are found in depressions; and the mill must, therefore, just as necessarily, be located at a higher level than its source of raw material, which involves increased expense in transporting the raw material to the mill.

Glacial clays, which are usually employed in connection with marl, commonly carry a much larger proportion of sand and pebbles than do the sedimentary clays of more southerly regions.

The effect of the water carried by the marl has been previously noted. The material as excavated will consist approximately of equal weights of lime carbonate and of water. This, on the face of it, would seem to be had enough as a business proposition; but we find that in practice more water is often added to permit the marl to be pumped to the mill.

On the arrival of the raw materials at the mill the clay is often dried, in order to simplify the calculation of the mixture. The reduction of the clay is commonly accomplished in a disintegrator or in edge-runner mills, after which the material is further reduced in a pug mill, sufficient water being here added to enable it to be pumped readily. It is then ready for mixture with the marl, which at some point in its course has been screened to remove stones, wood, etc., as far as possible. The slurry is further ground in pug mills or wet grinding mills of the disk type; while the final reduction takes place commonly in wet tube mills. The slurry, now containing 30 to 40 per cent of solid matter and 70 to 60 per cent of water, is pumped into storage tanks, where it is kept in constant agitation to avoid settling. Analyses of the slurry are taken at this point, and the mixture in the tanks is corrected if found to be of unsatisfactory composition. After standardizing, the slurry is pumped into the rotary kilns. Owing to the large percentage of water contained in the slurry the fuel consumption per barrel of finished cement is 30 to 50 per cent greater, and the output of each kiln correspondingly less than in the case of a dry mixture.

It may be of interest, for comparison with the above description of the wet process with rotary kilns, to insert a description of the semi-wet process as carried on a few years ago at the dome kiln plant of the Empire Portland Cement Company of Warners, N. Y. The plant has been remodeled since that date, but the processes formerly followed are still of interest, as they resulted in a high grade though expensive product.

At the Empire plaut the marl and clay are obtained from a swamp about three-fourths of a mile from the mill. A revolving derrick with elam-shell bucket was employed for excavating the marl, while the clay was dug with shovels. The materials were taken to the works over a private narrow-gauge road, on cars carrying about three tons each, drawn by a small locomotive. At the mill the cars were hanled up an inclined track, by means of a cable and drum, to the mixing floor.

The clay was dried in the Cummer "salamander" driers, after which it was allowed to cool, and then carried to the mills. These mills were the Sturtevant "rock emery" type, and reduced the clay to a fine powder, in which condition it was fed, after being weighed, to the mixer. The marl was weighed and sent directly to the mixer, no preliminary treatment being necessary. The average charge was about 25 per cent clay and about 75 per cent marl.

The mixing was carried on in a mixing pan twelve feet in diameter, in which two large rolls, each about five feet in diameter and sixteen-inch face, ground and mixed the materials thoroughly. The mixture was then sampled and analyzed, after which it was carried by a belt conveyor to two pug mills, where the mixing was completed and the slurry formed into slabs about three feet long and four to five inches in width and height. These on issuing from the pug mill were cut into a number of sections so as to give bricks about six inches by

four inches by four inches in size. The bricks were then placed on slats, which were loaded on rack cars and run into the drying tunnels. The tunnels were heated by waste gases from the kilns and required from twenty-four to thirty-six hours to dry the bricks.

After drying, the bricks were fed into dome kilns, twenty of which were in use, being charged with alternate layers of coke and slurry bricks. The coke charge for a kiln was about four or five tons and this produced twenty to twenty-six tons of clinker at each burning, thus giving a fuel consumption of about 20 per cent, as compared with the 40 per cent or so required in the rotary kilns using wet materials. From thirtysix to forty hours were required for burning the charge. After cooling, the clinker was shoveled out, picked over by hand, and reduced in a Blake crusher, Smidth ball mills, and Davidsen tube mills.

Composition of mixture.—The cement mixture ready for burning will commonly contain from 74 to 77.5 per cent of lime carbonate, or an equivalent proportion of lime oxide. Several analyses of actual cement mixtures are given in the following table. Analysis No. 1, with its relatively high percentage of magnesia, is fairly typical of Lehigh Valley practice. Analyses Nos. 2 and 3 show mixtures low in lime, while analysis No. 4 is probably the best proportion of the four, especially in regard to the ratio between silica and alumina plus iron. This ratio, for ordinary purposes, should be about 3:1, as the cement becomes quicker setting and lower in ultimate strength as the percentage of alumina increases. If the alumina percentage be carried too high, moreover, the mixture will give a fusible, sticky clinker when burned, causing trouble in the kilns.

	1	2	3	4
Silica (SiO_2)	12.626:0075.462.65	13.46	13.85	14.77
Alumina and Iron oxide $(Al_2O_3 + Fe_2O_3)$?	7.20	4.35
Carbonate of lime $(CaCO_3)$		73.66	73.93	76.84
Magnesium oxide (MgO)		?	?	1.74

Analyses of cement mixtures.

BURNING THE MIXTURE.

After the cement mixture has been carefully prepared, as described in preceding pages, it must be burned with equal care.

In the early days of the industry a simple vertical kiln, much like that used for burning lime and natural cement, was used for burning the Portland cement mixture. These kilns, while fairly efficient so far as fuel consumption was concerned, were expensive in labor, and their daily output was small. In France and Germany they were soon supplanted by improved types, but still stationary and vertical, which gave very much lower fuel consumption. In America, however, where labor is expensive while fuel is comparatively cheap, an entirely different style of kiln has been evolved. This is the rotary kiln. With the exception of a very few of the older plants, which have retained vertical kilns, all American Portland cement plants are now equipped with rotary kilns.

The history of the gradual evolution of the rotary kiln is of great interest, but as the subject can not be taken up here, reference should be made to the papers cited below^{*} in which details, accompanied often by illustrations of early types of rotary kilns, are given.

The design, construction and operation of the vertical stationary kilns of various types is discussed in many reports on Portland cement, the most satisfactory single paper being probably that referred to below. † As the subject is, in America at least, a matter simply of historical interest, no description of these kilns or their operation will be given in the present paper.

At present, practice in burning at the different American cement plants is rapidly approaching uniformity, though difference in materials, etc., will always prevent absolute uniformity from

^{*} Duryee, E., The first manufacture of Portland cement by the direct rotary kiln pro-cess. Engineering News, July 26, 1900. Leslie, R. W., History of the Portland cement industry in the United States, 146 pages, Philadelphia, 1900. Lewis, F. H., The American rotary kiln process for Portland cement; Cement Industry, pp. 188-199, New York, 1900. Matthey, H., The invention of the new cement-burning method. Engineering and Mining Journal, Vol. 67, pp. 555, 705, 1849. Stanger, W. H., and Blount, B., The rotary process of cement manufacture. Proc. Institute Civil Engineers, Vol. 145, pp. 44-136, 1901. Editorial, The influence of the rotary kiln on the development of Portland cement manu-facture in America. Engineering News, May 3, 1900. * Duryee, E., The first manufacture of Portland cement by the direct rotary kiln pro-

[†] Stanger, W. H., and Blount, B., Gilbert, W., Candlot, E., and others (Discussion of the value, design and results obtained from various types of fixed kilns). Proc. Institute Civil Engineers, Vol. 145, pp. 44-48, 81-82, 95-100. 1901.

being reached. The kiln in which the material is burned is now almost invariably of the rotary type, the rotary process, which is essentially American in its development, being based upon the substitution of machines for hand labor wherever possible. A brief summary of the process will first be given, after which certain subjects of interest will be taken up in more detail.

SUMMARY OF BURNING PROCESS.

As at present used, the rotary kiln is a steel cylinder from about six to eight feet in diameter; its length, for dry materials, has usually been sixty feet, but during the past year many eightyfoot, one hundred-foot and even longer, kilns are frequently employed.

This cylinder is set in a slightly inclined position, the inclination being approximately one-half inch to the foot. The kiln is lined, except near the upper end, with very resistant fire brick, to withstand both the high temperature to which its inner surface is subjected and also the destructive action of the molten clinker.

The cement mixture is fed in at the upper end of the kiln, while fuel (which may be either powdered coal, oil, or gas) is injected at its lower end. The kiln, which rests upon geared bearings, is slowly revolved about its axis. This revolution, in connection with the inclination at which the eylinder is set, gradually carries the cement mixture to the lower end of the kiln. In the course of this journey the intense heat generated by the burning fuel first drives off the water and carbon dioxide from the mixture, and then causes the lime, silica, alumina and iron to combine chemically to form the partially fused mass known as "cement clinker." This clinker drops out of the lower end of the kiln, is cooled so as to prevent injury to the grinding machinery, and is then sent to the grinding mills.

THEORETICAL FUEL REQUIREMENTS.

As a preliminary to a discussion of actual practice in the matter of fuel, it will be of interest to determine the heat units and fuel theoretically required in the manufacture of Portland cement from a dry mixture of normal composition.

In burning such a mixture to a clinker, practically all of the heat consumed in the operation will be that required for the dissociation of the lime carbonate present into lime oxide and carbon dioxide. Driving off the water of combination that is chemically held by the clay or shale, and decomposing any calcium sulphate (gypsum) that may be present in the raw materials, will require a small additional amount of heat. The amount required for these purposes is not accurately known, however, but is probably so small that it will be more or less entirely offset by the heat which will be liberated during the combination of the lime with the silica and alumina. We may, therefore, without sensible error, regard the total heat theoretically required for the production of a barrel of Portland cement as being that which is necessary for the dissociation of 450 pounds of lime carbonate. With coal of a thermal value of 13,500 B. T. U., burned with only the air supply demanded by theory, this dissociation will require 251_2 pounds of coal per barrel of cement, a fuel consumption of only 6.6 per cent.

LOSSES OF HEAT IN PRACTICE.

In practice with the rotary kiln, however, there are a number of distinct sources of loss of heat, which result in a fuel consumption immensely greater than the theoretical requirements given above. The more important of these sources of loss are the following:

1. The kiln gases are discharged at a temperature much above that of the atmosphere, ranging from 300° F. to 2,000° F., according to the type of materials used and the length of the kiln.

2. The clinker is discharged at a temperature varying from 300° F. to 2,500 F. the vange depending, as before, on materials and length of the kiln.

3. The air supply injected into the kiln is always greater, and usually very much greater, than that required for the perfect combustion of the fuel; and the available heating power of the fuel is thereby reduced.

4. Heat is lost by radiation from the ends and exposed surfaces of the kiln.

5. The mixture, in plants using a wet process, carries a high percentage of water, which must be driven off.

It is evident, therefore, that present-day working conditions serve to increase greatly the amount of fuel actually necessary

5

for the production of a barrel of cement above that required by theory.

ACTUAL FUEL REQUIREMENTS AND OUTPUT.

Rotary kilns are nominally rated at a production of 200 barrels per day per kiln. Even on dry and easily clinkered materials and with good coal, however, such an output is not commonly attained. Normally a kiln working a dry mixture will produce from 160 to 180 barrels of cement per day of twenty-four hours. In doing this, if good coal is used its fuel consumption will commonly be from 120 to 140 pounds of coal per barrel of cement, though it may range as high as 160 pounds, and, on the other hand, has fallen as low as 90 pounds. An output of 175 barrels per day, with a coal consumption of 130 pounds per barrel, may therefore be considered as representing the results of fairly good practice on dry materials. In dealing with a wet mixture, which may carry anywhere from 30 to 70 per cent of water, the results are more variable, though always worse than with dry materials. In working a sixty-foot kiln on a wet material, the output may range from 80 to 140 barrels per day, with a fuel consumption of from 150 to 230 pounds per barrel. Using a longer kiln, partly drying the mixture, and utilizing waste heat, will of course improve these figures materially.

When the heavy Western oils are used for kiln fuel, it may be considered that one gallon of oil is equivalent in the kiln to about ten pounds of coal. The fuel consumption, using dry materials, will range between eleven and fourteen gallons of oil per barrel of cement; but the output per day is always somewhat less with oil fuel than where coal is used.

Natural gas in the kilu may be compared with good Pennsylvania coal by allowing about 20,000 to 30,000 cubic feet of gas as equivalent to a ton of coal. This estimate is, however, based upon too few data to be as close as those above given for oil or coal.

EFFECT OF COMPOSITION ON BURNING.

The differences in composition between Portland cement mixtures are very slight if compared, for example, with the differences between various natural cement rocks. But even such slight differences as do exist exercise a very appreciable effect on the burning of the mixture. Other things being equal, any increase in the percentage of lime in the mixture will necessitate a higher temperature in order to get an equally sound cement. A mixture which will give cement carrying 59 per cent of lime, for example, will require much less thorough burning than would a mixture designed to give a cement with 64 per cent of lime.

With equal line percentages, the cement carrying high silica and low alumina and iron will require a higher temperature than if it were lower in silica and higher in alumina and iron. But, on the other hand, if the alumina and iron are carried too high, the clinker will ball up in the kiln, forming sticky and unmanageable masses.

CHARACTER OF KILN COAL.

The fuel most commonly used in modern rotary kiln practice is bituminous coal, pulverized very finely. Coal for this purpose should be high in volatile matter, and as low in ash and sulphur as possible. Rusell gives the following analyses of West Virginia and Pennsylvania coals used at present at various cement plants in Michigan:

	1	2	3	4
Fixed carbon	56.15	56.33	55.82	51.69
Volatile matter	35.41	35.26	39.37	39.52
Ash Maisture	6.36 2.08	7.06	3.81	6.13
Sulphur	1.30	1.34	0.42	1.46

Analyses of kiln coals.

The coal as usually bought is either "slack" or "run of mine." In the latter case it is necessary to crush the lumps before proceeding further with the preparation of the coal, but with slack this preliminary crushing is not necessary, and the material can go directly to the dryer.

DRYING COAL.

Coal as bought may carry as high as 15 per cent of water in winter or wet season. Uusally it will run from 3 to 8 per cent. To secure good results from the crushing machinery it is necessary that this water should be driven off. For coal drying, as for the drying of raw materials, the rotary dryer seems best

adapted to American conditions. It should be said, however, that in drying coal it is usually considered inadvisable to allow the products of combustion to pass through the cylinder in which the coal is being dried. This restriction serves to decrease slightly the possible economy of the dryer, but an evaporation of six to eight pounds of water per pound of fuel coal can still be counted on with any good dryer. The fuel cost of drying coal containing 8 per cent of moisture, allowing \$2 per ton for the coal used as fuel, will therefore be about three to four cents per ton of dried product.

PULVERIZING COAL.

Though apparently brittle enough when in large lumps, coal is a difficult material to pulverize finely. For cement kiln use, the fineness of reduction is very variable. The finer the coal is pulverized the better results will be obtained from it in the kiln; and the poorer the quality of the coal the finer it is necessary to pulverize it. The fineness attained in practice may therefore vary from 85 per cent, through a 100-mesh sieve, to 95 per cent or more, through the same. At one plant a very poor but cheap coal is pulverized to pass 98 per cent through a 100-mesh sieve, and in consequence gives very good results in the kiln.

Coal pulverizing is usually carried on in two stages, the material being first crushed to 20 to 30-mesh in a Williams mill or ball mill, and finally reduced in a tube mill. At many plants, however, the entire reduction takes place in one stage, Griffin or Huntington mills being used.

TOTAL COST OF COAL PREPARATION.

The total cost of crushing (if necessary), drying and pulverizing coal, and of conveying and feeding the product to the kiln, together with fair allowances for replacements and repairs, and for interest on the plant, will probably range from about twenty to thirty cents per ton of dried coal, for a 4-kiln plant. This will be equivalent to a cost of from three to five cents per barrel of cement. While this may seem a heavy addition to the cost of cement manufacture, it should be remembered that careful drying and fine pulverizing enable the manufacturer to use much poorer—and therefore cheaper—grades of coal than could otherwise be utilized.

CLINKER GRINDING.

The power and machinery required for pulverizing the clinker at a Portland cement plant using the dry process of manufacture is very nearly the same as that required for pulverizing the raw materials for the same output. This may seem, at first sight, improbable, for Portland cement clinker is much harder to grind than any possible combination of raw materials; but it must be remembered that for every barrel of cement produced about 600 pounds of raw materials must be pulverized, while only a scant 400 pounds of clinker will be treated, and that the large crushers required for some raw materials can be dispensed with in crushing clinker. With this exception, the raw material side and the clinker side of a dry-process Portland cement plant are usually abnost or exactly duplicates.

The difficulty, and in consequence the expense, of grinding clinker will depend in large part on the chemical composition of the clinker and on the temperature at which it has been burned. The difficulty of grinding, for example, increases with the percentage of lime carried by the clinker; and a clinker containing 64 per cent of lime will be very noticeably more resistant to pulverizing than one carrying 62 per cent of lime So far as regards burning, it may be said in general that the more thoroughly burned the clinker the more difficult it will be to grind, assuming that its chemical composition remains the same.

The tendency among engineers at present is to demand more finely ground cement. While this demand is doubtless justified by the results of comparative tests of finely and coarsely ground cements, it must be borne in mind that any increase in fineness of grinding means a decrease in the product per hour of the grinding mills employed, and a consequent increase in the cost of cement. At some point in the process, therefore, the gain in strength due to fineness of grinding will be counter-balanced by the increased cost of manufacturing the more finely ground product.

The increase in the required fineness has been gradual but steady during recent years. Most specifications now require at least 90 per cent to pass a 100-mesh sieve; a number require 92 per cent; while a few important specifications require 95 per cent. Within a few years it is probable that almost all specifications will go as high as this.

ADDITION OF GYPSUM.

The cement produced by the rotary kiln is invariably naturally so quick-setting as to require the addition of sulphate of lime. This substance, when added in quantities up to $2\frac{1}{2}$ or 3 per cent, retards the rate of set of the cement proportionately, and appears to exert no injurious influence on the strength of the cement. In amounts above 3 per cent, however, its retarding influence seems to become at least doubtful, while a decided weakening of the cement is noticeable.

Sulphate of lime may be added in one of two forms, either as crude gypsum or as burned plaster. Crude gypsum is a natural hydrous lime sulphate, containing about 80 per cent of lime sulphate and 20 per cent of water. When gypsum is calcined at temperatures not exceeding 400° F., most of its contained water is driven off. The "plaster" remaining carries about 93 per cent of lime sulphate, with only 7 per cent of water.

In Portland cement manufacture either gypsum or burned plaster may be used to retard the set of the cement. As a matter of fact, gypsum is the form almost universally employed in the United States. This is merely a question of cost. It is true, that to secure the same amount of retardation of set it will be necessary to add a little more gypsum than if burned plaster were used; but, on the other hand, gypsum is much cheaper than burned plaster.

The addition of the gypsum to the clinker is usually made before it has passed into the ball mill, komminuter, or whatever mill is in use for preliminary grinding. Adding it at this point secures much more thorough mixing and pulverizing than if the mixture were made later in the process. At some of the few plants which use plaster instead of gypsum, the finely ground plaster is not added until the clinker has received its final grinding and is ready for storage or packing.

CONSTITUTION OF PORTLAND CEMENT.

Constitution of Portland Cement.

During recent years much attention has been paid by various investigators to the constitution of Portland cement. The chemical composition of any particular sample can, of course, be readily determined by analysis, and by comparison of a number of such analyses, general statements can be framed as to the range in composition of good Portland cements.

The chemical analysis will determine what ingredients are present, and in what percentages, but other methods of investigation are necessary to ascertain in what manner these various ingredients are combined. A summary only of the more important results brought out by these investigations on the constitution of Portland cement will be given in this place.

It would seem to be firmly established that, in a well burned Portland cement, much of the lime is combined with most of the silica to form the compound 3 CaO. SiO_2 , tricalcic silicate. To this compound are ascribed, in large measure, the hydraulic properties of the cement, and in general it may be said that the value of a Portland cement increases directly as the proportion of 3 CaO. SiO_2 . The ideal Portland cement, toward which cements as actually made tend in composition, would consist exclusively of tricalcic silicate, and would be, therefore, composed entirely of lime and silica, in the following proportions:

Lime	(CaO)															73.6	
Silica	(SiO_2)					•				•						26.4	

Such an ideal cement, however, can not be manufactured under present commercial conditions, for the heat required to clinker such a mixture can not be attained in any working kiln. Newberry has prepared such mixtures by using the oxy-hydrogen blowpipe; and the electrical furnace will also give clinker of this composition; but a pure lime-silica Portland is not possible under present day conditions.

In order to prepare Portland cement in actual practice, therefore, it is necessary that some other ingredient or ingredients should be present to serve as a flux in aiding the combination of the lime and silica, and such aid is afforded by the presence of alumina and iron oxide.

Alumina (Al_2O_3) and iron oxide (Fe_2O_3) , when present in noticeable percentages, serve to reduce the temperature at which combination of the lime and silica (to form 3 CaO. SiO_2) takes place; and this clinkering temperature becomes further and further lowered as the percentages of alumina and iron are increased. The strength and value of the product, however, also decrease as the alumina and iron increase; so that in actual practice it is necessary to strike a balance between the advantage of low clinkering temperature and the disadvantage of weak cement, and to thus determine how much alumina and iron should be used in the mixture. Alumina affects the initial setting of cement, high alumina producing rapid while low alumina produces slow setting. It is advisable to keep the alumina as low as possible, but high enough to secure a proper clinkering temperature. High alumina causes a fusible sticky clinker liable to ball up in the kiln. Le Chatelier considers the alumina compounds in Portland cement the cause of its disintegration by sea water, the action being as follows:

The hardening of cement liberates free lime which reacts with the magnesium sulphate always present in sea-water to form calcium sulphate. This in turn reacts with the calcium aluminate of the cement to form sulph-aluminate of lime, a compound that swells on hydration, thus disintegrating the whole mass.

It is generally considered that whatever alumina is present in the cement is combined with part of the lime to form the compound 2 CaO. Al_2O_3 , dicalcic aluminate. It is also held by some, but this fact is somewhat less firmly established than the last, that the iron present is combined with the lime to form the compound 2 CaO. Fe_2O_3 . Iron oxide in less amounts than 4 to 6 per cent is usually calculated as alumina, but if more is present, the difference in their combining weights must be allowed for. It decreases the clinkering temperature but differs from alumina in giving a slower setting cement. The darker colors of cements are usually produced by the iron oxide contained.

The European limit for magnesia is 3 per cent but good Portlands are made in the Lehigh Valley region with 4 to 5 per cent. Professor S. B. Newberry has proved that good cements can

TESTING OF RAW MATERIALS.

be made carrying 10 per cent magnesia if due care be exercised in mixing and burning. Magnesia is regarded by some as equivalent in its behavior to lime and within limits it can be used to replace the latter if allowance be made for the difference in their combining weights. It is theoretically possible to prepare a series of lime-magnesia cements parallel to Portland cements as now made. These will differ in quality and behavior and would not be properly classified with Portlands. The amount of magnesia in Portland cement is now generally restricted to less than 5 per cent. Its detrimental effect takes place after the calcium compounds have hydrated and thus causes expansion which tends to destroy the structure of the cement.

Sulphur may occur as sulphate or sulphide. In the rotary kiln, the usual oxidizing flame dissociates sulphates as follows: $CaSO_4 + heat = CaO + SO_3$. The SO₃ passes off as gas. If the flame is not sufficiently oxidizing, the CaSO₄ may be reduced to sulphide form.

Alkalies in small per cents have been considered detrimental by some, inert or beneficial by others, but their effect is not well known. The rate of setting is hastened by addition of alkali solutions. Most of the alkali in the raw mixture is probably volatilized during the burning and would form a valuable byproduct if recovered from the flue gases.

Phosphorus is seldom found in cement materials except marl. Its effect on cement is not definitely known, but is supposed to cause an increase in the tensile strength at first but a loss when the cement is older.

TESTING OF RAW MATERIALS TO DETERMINE AVAIL-ABILITY FOR THE MANUFACTURE OF PORTLAND CEMENT.

As is pointed out in preceding paragraphs, the natural deposits from which Portland cement is made comprise limestone, chalk or marl and clay or shale. In the exploitation of these raw materials there are a number of factors to be taken into consideration. The more important of these are enumerated on page 50. Whether given beds are suitable, depends pri-

marily on their chemical composition and physical characteristics. Should these properties prove favorable, the extent of the deposits, that is, the quantity of the raw materials available, must be ascertained, before the strictly commercial and economic relations, transportation facilities, fuel supply and markets, are brought under serious consideration.

Evidently, the location of the proper materials is the first step in exploitation. At the same time, the commercial factors must be kept in mind, for it would be useless to prospect for cement-making materials, as for any other economic product, in regions which, because of their remoteness, preclude utilization or development. Recalling, however, the fact that Portland cement requires limestone and clay in about the proportion of 3 to 1, it is apparent that both ingredients need not be found in immediate proximity to each other. It is not unusual for cement plants to locate at the source of the lime, the clay or shale being transported for considerable distances. Suitable limestone, therefore, is the first essential, after which a clay or shale must be found that will give a proper cement mixture in combination with the limestone.

It is rarely, if ever, the case that investigators are equipped with the necessary apparatus for making practical tests of favorable materials. Such tests would include fine grinding, mixing and burning to clinker, besides pulverization of the burned cement and testing the setting properties of the product. In fact, there are few laboratories in this country where tests of this nature are carried out. Investigations of Portland cement materials have, up to the present, been limited substantially to chemical and physical tests of the separate raw ingredients, drawing conclusions from these as to their suitability; the final and only absolutely conclusive test being performed on a large scale in the completely equipped factory.

It has proven a problem of some magnitude to devise equipment with which can be initated on a small scale the conditions to which cement materials are subjected in the factory. Burning tests have been especially troublesome, the designing of a small kiln in which the conditions could be accurately controlled and the necessary elevated temperatures produced, meeting with varying degrees of success. It is, without doubt, due to the difficulties encountered in making the practical tests that more attention has been given to indirect methods of experiment. Experience has shown that not only must the limestone and shale be blended in certain proportions but that the various elements in the shale, especially, must be present in amounts bearing definite relations to each other or the proper mixture with the limestone is impossible. These factors depend alone on chemical composition. But the physical condition of the mineral particles composing the clay, and the limestone, if it be impure, is of equal importance. Of two clays with identical ultimate chemical composition, one might be eminently suitable and the second much less so or even valueless for making cement, on account of their dissimilar physical make-up.

In general, the finer the grain of the clay and of the impurities in the source of the lime, the more favorable are the materials for cement purposes. Size of grain is not, however, the only physical factor to be taken into account. Since the burning of cement brings about a chemical union of the lime with the silica, alumina and iron, the susceptibility of these latter compounds to the attack of the lime is of great importance. Free silica in the shape of crystalline quartz sand if very fine, is readily attacked at high temperatures. If the silica be present, however, in the non-crystalline or colloid condition, or in combination with alkalis or alkaline earths as in the feldspars, or with alumina as in clav itself, the size of grain may be considerably larger and chemical combination in burning proceed with equal facility. Silica or silicates which are thus susceptible to the action of caustic line are said to be "unlocked," and the silica in a seminascent condition. Silica is the most important ingredient to be considered in this connection, but similar statements will apply in some degree to the iron oxide and alumina as well.

The chemical stability of the elements in the mixture should therefore be taken into account along with the size of grain, and the first factor may properly be referred to as a chemico-physical one.

The foregoing statements may perhaps suggest two principal lines of investigation to be applied to possible cement materials.

First, the ultimate chemical analysis of both classes of ingredients, the limestone or marl and the clay; second, an inquiry into, or a determination of, the susceptibility to attack by lime of the clay and other siliceous components. These two lines of procedure have been attempted, supplemented in some instances by actual burning tests. In the remaining portions of this chapter the methods employed are explained and some results are given.

Methods of Testing.

As has been shown, chemical composition is the necessary basis for scientific cement manufacture. A statement of the chemical analysis of each of the ingredients is essential in order that proper and uniform mixtures may be compounded. All experimental work to determine the value of cement materials must, as well, depend on a correct knowledge of the elements composing them. The chemical analysis affords a means of comparison of promising new materials with others now in use.

THE ANALYSIS OF LIMESTONES.*

The constituents to be determined are the insoluble siliceous matter, oxide of iron and aluminum, carbonate of lime and carbonate of magnesia. The siliceous matter consists of sand (silica) and silicates, chiefly clay (silicate of alumina).

Process of Analysis.—Weigh 1g. of the finely ground sample. Transfer it to a 4-in. casserole or dish, cover with a watch glass, add 25 to 30 c.c. of water, then 15 c.c. of concentrated HCl, and warm until all effervescence has ceased. Remove the cover, wash it off into the dish, add 4 to 5 drops of HNO₃ and evaporate the solution to dryness on a water bath or hot plate; or replace the cover and boil down directly over the lamp, using constant care to prevent loss by "spattering"; finally heat very carefully over the lamp flame until all odor of HCl is gone. The temperature attained should not exceed 120° C. It can be regulated by drying in an air bath, but the "trick" of doing it as indicated is soon learned and saves much time. Now cool, add 5 c.c. of HCl, warm till the Fe salts are dissolved, add 50 c.c. of water and heat until everything dissolves except the siliceous matter, which forms a flocculent or sandy residue. Fil-

^{*}Notes on Metallurgical Analysis, N. W. Lord. 2d Ed., 1903, p. 16.

ter through a 5 or 7 cm. filter, and wash thoroughly with hot water until a few drops of the washings show no reaction for HCl when tested with $AgNO_3$.

Ignite and weigh the residue, which, after deducting the weight of the filter ash, constitutes the "insoluble siliceous matter." Keep it for the determination of the silica by fusion.

To the filtrate, the volume of which should be about 100 c.c., carefully add NH₄OH until it just smells distinctly of NH₅. Should the precipitate be light colored and large in amount, indicating the probable precipitation of Mg(OH)₂, add 5 c.c. HCl and again NH₄OH as before. Now boil the liquid about five minutes or until the odor of NH₅ has nearly gone—maintaining the volume of the liquid if necessary by adding water from time to time. Remove the lamp, and let the precipitate settle, filter into a small filter, wash well with hot water, ignite and weigh the precipitate of Fe₂O₃ + Al₂O₅.

The Fe_2O_3 and P_2O_5 may be determined in another portion, and when deducted from the above will give the alumina by difference.

Dilute the filtrate to about 200 c.c. If it is not distinctly alkaline add five to ten drops of NH₄OH, heat to boiling and slowly add 80 c.e. of a solution of $(NH_4)_2 C_2O_4$ heated to boiling point also. Use a saturated solution of the salt diluted with an equal volume of water. Stir well during the addition of the reagent and for a minute or two afterwards, then set aside until the precipitate of CaC_2O_4 has settled completely. Decant the liquid through a 9 cm. filter without disturbing the precipitate, wash the precipitate once or twice by decantation, using about 100 c.e. of boiling water each time, then transfer it to the filter and wash 6 or 7 times with hot water. When the filtrate is to be concentrated for the determination of the magnesia, set aside the first filtrate and decantation and catch the subsequent washings in a separate beaker. Concentrate these by boiling down to a small volume and then add them to the first portion.

Dry the precipitate thoroughly, detach it as far as possible from the filter, put it in a weighed No. 0 porcelain crucible, burn the filter carefully on a platinum wire and add the ash to contents of the crucible. Now drop concentrated H_2SO_4 on to the precipitate till it is well moistened, but avoid much excess.

Heat the crucible (working under a "hood" to carry off the fumes) holding the burner in the hand and applying the flame cautiously until the swelling of the mass subsides, and the excess of H_2SO_4 has been driven off as white fumes. Finally heat to a cherry red for 5 minutes. Do not use the blast lamp. Cool and weigh the CaSO₄. The weight of the CaSO₄ multiplied by 0.735 gives the amount of CaCO₃ in the sample. The filtrate from the CaC_2O_4 should be, if over that volume, concentrated by boiling to 300 c.c.; should any MgC_2O_4 separate, dissolve it by adding a little HCl. Cool, add NH,OH till alkaline, then add 10 c.c. or a sufficient quantity of a saturated solution of Na_2HPO_4 . Then add gradually 1-10 of the volume of the liquid of strong NH₄OH, (sp. gr. 0.90) stir hard for some time, cover and let settle until the liquid is perfectly clear (about 2 hours), filter and wash with water containing 1-10 of its volume of strong NH₄OH and a little NH₄NO₃. Ten c.c. of the phosphate solution is sufficient for about 20 per cent of $MgCO_3$; for dolomites more must be added. Dry the precipitate, detach it from the filter and burn the filter on a platinum wire; now ignite precipitate and filter ash in a porcelain crucible, first heating carefully over a Bunsen burner till all volatile matter is driven off and it has been at a dull red heat for some minutes, then finishing over the blast lamp for five or ten minutes.

The ignited precipitate is $Mg_2P_2O_7$, the weight of which multiplied by 0.757 gives the $MgCO_3$ in the sample.

Treatment of the Siliceous Residue for the Determination of SiO_2 .—Mix the ignited residue with eight or ten times its weight of dry Na₂CO₃, in a platinum crucible of at least 15 c.c. capacity, heat it over a Bunsen burner until the mass has well caked together, then over a blast lamp until it is in quiet fusion. Now remove the crucible with a pair of tongs and dip the bottom in cold water, which will usually cause the mass to loosen.

Wash off any of the material spattered on the cover of the crucible into a casserole with hot water. Add the fused cake, if it has come loose; if not, fill the crucible with water and warm until the fused mass softens up and can be transferred to the casserole. Finally clean the crucible with hot water and add the washings. If any material adheres so as not to be removed by washing with water, dissolve it with a little HCl and add to the rest, (on no account punch or dig the material out, as this may ruin the crucible). When the fusion has been thoroughly disintegrated by the hot water and no hard lumps are left, add HCl until everything dissolves, cover the dish and warm till effervescence ceases. Remove and wash the cover and evaporate the solution to dryness on a water bath or otherwise; when dry and every trace of odor of HCl has gone, add 10 c.c. dilute HCl (1 : 1) and then 50 c.e. of water. Warm till the NaCl has dissolved, filter, wash well with hot water, dry and ignite the residual SiO₂. The ignition must be repeated and the residue reweighed until its weight does not change.

In the filtrate the iron, alumina, lime and magnesia may be determined as in the regular process, and the amounts so found added to the weight of the main precipitates.

THE ANALYSIS OF CLAYS.*

Fuse 1 gram of the finely ground clay, dried at 100° C., with 10 grams of sodium carbonate and a very little sodium nitrate. Run the fused mass well up on the sides of the crucible, allow it to cool, and treat it with hot water until thoroughly disintegrated, transferring the liquid from time to time to a platinum dish. Treat the crucible with hydrochloric acid, add this to the liquid in the dish, acidulate with hydrochloric acid, and evaporate to dryness in the air-bath. Treat the mass with water and a little hydrochloric acid, evaporate again to dryness, and treat with 15 c.c. hydrochloric acid and 45 c.c. water. Allow it to stand in a warm place for fifteen or twenty minutes, add 50 c.e. water, and stand in a warm place for fifteen or twenty minutes, add 50 c.c. water, and filter on an ashless filter. Wash thoroughly with hot water acidulated with a few drops of hydrochloric acid, dry, ignite, heat for three or four minutes over the blast-lamp, and weigh. Treat the precipitate with hydrofluoric acid and a few drops of sulphuric acid, evaporate to dryness, ignite, and weigh. The difference between the two weights is silica. If any appreciable residue remains in the crucible, treat it with a little hydrochloric acid, and wash it out into the filtrate from the silica. Transfer the filtrate from the silica to a large platinum dish, heat it to boiling, add an

^{*}Blair's Chemical Analysis lron, 6th Ed. 1906, p. 278.

excess of ammonia, boil until the smell of ammonia is quite faint, filter on an ashless filter, and wash several times with hot water. Stand the filtrate and washings aside, and treat the precipitate on the filter with a mixture of 15 c.c. hydrochloric acid and 15 c.c. water (cold). Allow the solution to run into a small clean beaker, replace this by the platinum dish in which the precipitation was made, pour the solution on the filter again, and repeat this operation until the precipitate has completely dissolved. Riuse the beaker and wash the filter thoroughly with cold water, dry, and preserve it. Reprecipitate by ammonia, as above directed, filter on an ashless filter, wipe the dish with small pieces of filter-paper, add these to the precipitate, and wash thoroughly with hot water. Dry, ignite and precipitate and filter, and the filter from the first precipitation, heat for a few minutes over the blast-lamp, cool, and weigh as alumina and ferric oxide. Fuse the ignited precipitate with sodium carbonate, treat the fused mass with water, wash it into a small beaker, allow the residue to settle, decant off the clear, supernatant fluid, treat the residue with hydrochloric acid, and determine the iron volumetrically, or add citric acid and annuonia, and after precipitating the iron as sulphide, filter, wash, dissolve in hydrochloric acid, oxidize with brominewater, and precipitate the ferric oxide by ammonia. Filter, wash, dry, ignite, and weigh as ferric oxide. Subtract the weight of ferric oxide from the alumina plus ferric oxide found above, and the difference is alumina.

As the amounts of calcium and magnesium in clay are very small, the filtrate and washings from the second precipitation of alumina plus ferric oxide may be rejected and the lime and magnesia determined in the first filtrate as directed on page 77.

The J. Lawrence Smith process is standard for determining alkalis. Place 1 gram of the finely ground clay in a porcelain or agate mortar, add an equal weight of granular ammonium chloride, and grind the entire mass so as to obtain an intimate mixture of the whole. Transfer to a capacious platinum crucible, cover with a close-fitting lid, and heat carefully to decompose the ammonium chloride, which is accomplished in a few minutes. Heat gradually to redness, and keep the bottom of the crucible at a bright red for about an hour. Allow the crucible to cool, and if the mass is easily detached from the crucible, transfer it to a platinum dish and add about 80 c.c. of water. Wash the crucible and lid with boiling water, pouring washings into the dish. Heat the water in the dish to boiling, and, when the mass has completely slaked, filter into another platinum dish and wash the mass on the filter with hot water. If the semi-fused mass in the crucible is not easily detached, place the crucible on its side in the dish, add about 100 c.c. water, and heat until the mass disintegrates. Remove the crucible, rinse it, and filter as above directed. To the filtrate add about 1 1/2 grams of pure aumonium carbonate, evaporate on the water-bath, or very carefully over a light, until the volume of the solution is reduced to about 40 c.c., add a little more ammonium carbonate and a few drops of ammonia, and filter on a small filter. Evaporate the filtrate carefully after adding a few drops more of ammonium carbonate to make certain that all the lime has been precipitated. If any further precipitate appears, filter into a platinum crucible and evaporate to dryness. Heat carefully to dull redness to drive off any ammonium salts, and weigh the residue as potassium sodium chloride. To the residue in the crucible add a little water, in which the residue should dissolve perfectly, and a solution of platinic chloride. Evaporate down in the water-bath until the mass in the crucible solidifies upon cooling, add a little water to dissolve the excess of platinic chloride, and then an equal volume of alcohol.* Filter on a Gooch crucible, wash with alcohol until the filtrate runs through perfectly colorless, dry at 120° C., and weigh as potassium platinic chloride. This weight, multiplied by .19395, gives the Then multiply the weight of potassium weight of potash. platinic chloride by .30696, which gives the weight of potassium chloride. Subtract this from the weight of potassium chloride plus sodium chloride previously obtained, and the difference is the weight of sodium chloride which, multiplied by .53077, gives the weight of soda.

^{*}The strength of the alcohol is important. The K2PtCls is practically insoluble in 80 per cent alcohol, but the Na2PtCls will dissolve in it. Time must be given to secure complete solution of this latter salt. Lord's Metallurgical Notes, Ed. 1903, p. 208.

Determine the water of composition by igniting 1 gram of the clay for twenty minutes at a bright red heat, when the loss of weight will represent the water.

INTERPRETATION OF ANALYSES.

The point in an analysis of a clay to which attention should first be given is the relation between the percentage of silica and the sum of the alumina and the iron oxide. Experience has shown that,

$$\frac{\rm SiO_2}{\rm Al_2O_3\,+\,Fe_2O_3} \ {\rm should} \ {\rm be} < \ 3.57 \ {\rm and} > \ 2.0,$$

in order that a proper mixture may be made with a pure limestone. The magnesia must not run over 5 to 6 per cent. The allowable maximum of alkalis and sulphur is 3 per cent. Texturally the clay should be fine-grained, and contain less than one per cent of free silica as sand or chert, since particles larger than 150-mesh will not easily enter into combination with lime.

So far as the complete chemical analysis tells us, we learn nothing of the state of combination in which any of the oxides determined exist. It is especially necessary to know whether the silica is present in available condition to combine with lime in burning. The decomposition of silicates by heating with lime carbonate to a red heat is practiced in quantitative analysis in the determination of alkalis in silicates by the J. L. Smith process. This principle has been applied by Professor Lunge and Dr. Schochor in Germany in the investigation of marls for cement manufacture. They showed that lime attacks most readily the combined silica and that present in a fine state of division, and that an expression of the cement-making value of the marls might be thus obtained. Professor Edward Orton, Jr., has applied the same process to the investigation of clays^{*} by which means a value is obtained which may be termed the hydraulic factor. In Orton's work a fixed proportion of one part clay to four of pure CaCO₃ was employed and the mixture heated to 1100° C. for seventy-five minutes. The latter method with slight modifications has been used to test Iowa clays.

^{*}Bulletin No. 3, Ohio Geological Survey, p. 120 et seq.

It is evident that the knowledge gained from both the complete and the carbonate analysis is of much greater value than the results of either alone. So far as used, the Orton method is regarded as furnishing the most reliable obtainable data as to the availability of a clay, without an actual burning test. Practical application has not yet proven that clays which appear unfavorable under this treatment will be unsuitable as a cement material. A wider use will be required to demonstrate this point. It is known, however, that some clays that have tested favorably by the method have proved satisfactory in practice.

The tests made by the Ohio Geological Survey and the present experiments indicate that there is an intimate relation between the chemical and physical condition of the minerals composing clays and the value of the latter for cement manufacture. The carbonate analysis seems the most satisfactory means yet suggested of expressing this relation.

DETERMINATION OF HYDRAULIC FACTOR.

The clay to be tested was crushed to one-eighth inch in a small roll-jaw crusher. One hundred grams were weighed approximately and disintegrated by boiling. The sample was then put on a 40-mesh sieve. The over size was intimately mixed with that passing through the sieve before the sample for burning was taken. As it is essential that the natural grain of the clay be not altered, no pulverizing was done, except such as was necessary to break the lumps before screening, and this only with the fingers or by boiling and rubbing with a soft rubber pestle.

Two grams of the prepared clay were weighed on a watch glass and enough calcium carbonate added to make a mixture of one part clay to four parts $CaCO_3$. Absolutely exact proportions are found not to be necessary, so long as there is an excess of the carbonate. One to four is found ample, and in order to give the clays uniform and comparable treatment was adhered to throughout. Allowance was therefore made for the lime which is practically always present in clays in greater or less quantity. To illustrate the method of making this correction, suppose a clay contains five per cent $CaCO_3$. Two grams contain 0.1 g. of the carbonate.

2.0 - 0.1 = 1.9 grams of the other clay ingredients present.

 $1.9 \times 4 = 7.6$ grams of CaCO₃ required to make a 1 to 4 mixture.

7.6 - 0.1 = 7.5 grams of CaCO₅ required to add to 2 grams of the clay to make the desired mixture.

The calcium carbonate and clay were well mixed on glazed paper and placed in a 50 c.c. platinum crucible. Enough water was added to make a thin slip which was stirred and the mass evaporated to dryness. The burning was done over a blast lamp in a small cylindrical furnace of the Erdman type. It was found inconvenient to maintain as high a heat (1100° C.) as recommended by the Ohio Geological Survey. The temperature employed varied from 950° C. to 1060° C. and the heating continued for seventy minutes after the maximum temperature was reached.

The temperature to be used in the test should be sufficiently high to bring into soluble form the maximum amount of silicate and yet remain safely below the limit where sintering or actual clinkering begins. In the subsequent treatment with acid and alkali the mass should disintegrate completely, which would not be the case had chemical combination progressed to the fusing or slag stage. Temperatures below this limit will give relatively smaller amounts of soluble residue, but will afford results, nevertheless, that are strictly comparable for the clays treated.

After heating at the temperature stated for seventy minutes the mass was removed from the crucible and digested for five hours in hot dilute (1:3) hydrochloric acid. The insoluble matter was filtered out and treated with a ten per cent hot solution of Na₂CO₃ until no flocculent silica was observed on testing with ammonium chloride. The insoluble was given a final washing with twenty per cent hydrochloric acid solution, ignited and weighed. The weight of the undissolved residue divided by two (since two grams of clay were taken) gives the percentage of insoluble or the hydraulic factor.

The first trials of this method with Iowa clays are not strictly comparable with the Ohio Survey work since the conditions of burning were modified to some extent. The value of the results, therefore, can be determined by employing as a standard the

			CHEMICAL ANALYSES.											
	Si02	AlgOa	Fe2O3	CaO	MgO	K2O	Na ₂ 0	SOa	+ 0 ª H	—0±Ĥ	COs	$\frac{8i0_2}{Al_2O_3 + F}$	Hydraulic Factor	ANALYST.
Blue Shale-Mason City Yellow Shale-Mason City Shale-Decorah Shale-Flint Brick Co Shale-Fort Dodge Shale-Lebigh P. C. Co., Mitchell, Ind	51.95 54.56 17.45 63.75 70.20 59.64	18.34 16.32 5.57 19.87 16.70 19.14	$7.56 \\ 14.30 \\ 9.15 \\ 5.57 \\ 4.00 \\ 7.59$	$\begin{array}{r} 4.14 \\ 4.10 \\ 30.21 \\ 1.55 \\ .28 \\ .26 \end{array}$	3.26 2.13 1.95 1.22 .63 2.31	3. 2. 2. 2. 3. 4.	12 32 53 77 14 33	2.76 2.30 1.67 2.70 .83	7.39 4.19 5.57 0.6	.42 .30 .25 0. 36	$3.06 \\ 5.61 \\ 26.02 \\ 1.51 \\ 53 \\ .35$	2.01 1.78 1.17 2.50 3.40 2.23	.2645 .2375 .220 .273 .4690 .227	J. B, Weems. L. G. Michael. L. G. Michael. J. B. Weems. J. B. Weems. U. S. Geolog. Surv
Shale – Panora, Iowa	53.82 48.91 35.48 55.52	17.53 17.66 15.85 14.59	$5.65 \\ 6.62 \\ 5.43 \\ 9.09 \\ 6.00$	4.40 8.42 12.56 5.00	2.19 1.90 6.24 2.60	1.74 2.61 1.59 1.50	1.12 1.44 .26 1.32	3.34 .28 3.36 .28	 	2.62 1.60 1.88 1.39		2.32 2.01 1.66 2.30	.1053 .1149 .3298 .2809	Bull 243, p. 144. A. O. Anderson. A. O. Anderson. A. O. Anderson. C. C. Clauson. A. O. Anderson.

.

,

.

.

2

ş

38

figures obtained from tests of clays which are now in use and known to give satisfaction in the manufacture of standard brands of Portland cement. For this purpose a sample of the shale used at the Lehigh Cement Company's Mill C at Mitchell, Indiana, was similarly tested and the factor included in the table appended. It will be noted that the hydraulic factor runs, in those clays which were at all favorable, from .2645 to .22, while the Mitchell shale gave .227.

In a later series of tests made in 1907 somewhat more uniform temperatures were employed, ranging between 1000 and 1060° C. The results of these tests appear as the last five members in the appended table. It will be noted that the minimum value of the hydraulic factor is .1053, in the case of the shale from Panora, Iowa.

CALCULATION OF CEMENT MIXTURES.

Experience has shown that the raw materials for cement must be blended in certain proportions, which range within narrow limits, in order to produce a high grade and uniform product. These proportions depend on the results already obtained by chemical analysis of the clay and limestone or marl to be used and are calculated from the percentage compositions of these ingredients. A lack of agreement among investigators as to the final constitution of the cement clinker has given rise to somewhat varying methods of proportioning the ingredients in the raw mixture. The methods employed are best illustrated by examples. E. C. Eckel* expresses the relation between the argillaceous and calcareous materials by the following ratio which is termed the Cementation Index.

 $(2.8 \text{ x percentage silica } (\text{SiO}_2)) + (1.1 \text{ x percentage alumina } (\text{Al}_2 \text{ O}_3)) \text{ x } (.7 \times \text{percentage iron oxide } (\text{Fe}_2 \text{O}_3)).$

86

⁽Percentage lime (CaO)) + (1.4 x percentage magnesia (MgO)). *Cements, Limes and Plasters, Wiley & Sons, p. 391.

The proper proportions are present when this ratio is equal to unity. If the value falls below 1.0, free lime or magnesia will be present; if it rises above 1.0, there is a deficiency of lime. Based on the above relations the process of calculation would be as follows:

Analysis of Raw Materials.

SHALE FROM GLENDON, IOWA.	LIMESTONE FROM EARLHAM, IOWA.
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Insoluble siliceous

Operation 1. Multiply the percentage of silica in the clayey material by 2.8, the percentage of alumina by 1.1, and the percentage of iron oxide by 0.7; add the products; subtract from the sum thus obtained the percentage of lime oxide in the clayey material plus 1.4 times the percentage of magnesia and call the result n.

Operation 2. Multiply the percentage of silica in the calcareous material by 2.8, the percentage of alumina by 1.1, and the percentage of iron oxide by 0.7; add the products and subtract the sum from the percentage of lime oxide plus 1.4 times the percentage of magnesia in the calcareous material; call the result m.

Operation 3. Divide n by m. The quotient will be the number of parts of calcareous material required for one part of clayey material.

The clay:

$48.91 \times 2.8 = 136.95$
$17.66 \times 1.1 = 19.37$
$6.62 \times 0.7 = 4.63$
160.95
8.42
$1.90 \times 1.4 = 2.66$
11.08

160.95 - 11.08 = 149.87 = n.

The limestone:

(Siliceous matter) $7.85 \times 2.8 = 21.98$ (Alumina + iron oxide) $1.00 \times 1.1 = 1.10$

23.08

(Lime) (Magnesia) $.29 \times 1.4 = \frac{51.05}{.41}$

51.46 - 23.08 = 28.38 = m. Then,

 $\frac{n}{m} = \frac{149.87}{28.38} = 5.28$ parts limestone by weight to be used for each part of elay. In practice, it has been found best to reduce the

amount of limestone about ten per cent from that obtained by the formula since the latter stands for the highest quantity of lime that will theoretically combine with the clay.

Bleininger gives the following method of batch calculation.^{*} The Glendon shale and Earlham limestone whose analyses are given above are used.

The formula assumed for the burned product is: (2.8CaO) SiO₂. (2CaO) Al₂O₃, which requires for each part by weight of silica 4.66 parts of calcium carbonate, and for each part of alumina, two parts of the lime carbonate. Therefore,

(Silica) $48.91 \ge 4.66 = 227.92$ (Alumina + iron oxide) $24.28 \ge 2.00 = 48.56$

276.48 lime carbonate to

satisfy the silica and alumina of the clay.

The clay already contains 8.42 per cent CaO (= 15.03 calcium carbonate) which it will contribute to the mixture and which must therefore be subtracted. At the same time, the limestone contains silica, alumina and iron oxide which must be taken into account. We have therefore,

276.48 - 15.03 = 261.45 parts calcium carbonate to be added to the clay; and from limestone analysis, calcium carbonate, 91.15 (= 51.05×1.785) - ($7.85 \times 4.66 + 1.00 \times 2$) = 52.57.

 $7.85 \times 4.66 + 1.00 \times 2 = 38.58$ parts of lime carbonate that will combine with the other ingredients of the limestone.

Total lime carbonate in the limestone, 91.15 - 38.58 = 52.57 parts calcium carbonate available from the stone. 261.45 parts are

* Bulletin 3 (4th series), Ohio Geological Survey, p. 239.

required. The amount by weight of limestone for one part of clay is 261.45 divided by 52.57 = 4.97.

In the above calculations the magnesia is neglected and the ferric oxide is taken with the alumina. Where these constituents are low in amount such procedure is permissible but it has been shown that the influence of iron and magnesia is such that they should have separate consideration. They are thus comprehended in the formula given on page 85, and to this extent the first method of calculation is the more accurate.

The two methods given are applicable for determining the correct proportion in which to blend new and unused raw materials as well as a means of control over mixtures already in use. In the latter instance, however, more rapid means are commonly employed. Experience with given materials will determine the limits within which they may vary and still afford a satisfactory cement. The total amount of the lime and magnesium carbonates is frequently made the basis of control. Their percentages are quickly ascertained by the chemist and the limestone or marl and the clay apportioned accordingly. Bleininger^{*} gives the following formula for calculating the daily mixture after once the best proportion of a mixture has been established, which depends essentially on the calcium oxide in the raw materials:

Let x = weight of limestone in charge

y = weight of clay in charge

a = per cent of calcium oxide in the limestone

b = per cent of calcium oxide in the clay

c = per cent of calcium oxide in the mixture.

Then
$$c = \frac{ax + by}{x + y}$$
 or $x(a - c) = y$ (c - b) or $\frac{x}{y} = \frac{c - b}{a - c}$.

* Bulletin 3 (4th series), Ohio Geological Survey, p. 242.

.