
**CEMENT AND CEMENT MATERIALS
OF IOWA.**

BY

EDWIN C. ECKEL AND H. F. BAIN.

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INTRODUCTION.

BY H. FOSTER BAIN.

Cement is now one of the most important mineral resources of the United States. In the value of the annual output it ranks thirteenth. It is about equal to the zinc production if the latter be estimated at New York prices. The rapid increase in use, and growth of local production of cement in the last ten years have been among the most striking features of the American mineral industry. The following tables from the mineral resources for 1902, as prepared by L. L. Kimball of the United States Geological Survey, will give some idea of the present extent of the industry.

PRODUCTION OF CEMENT IN THE UNITED STATES.

The total production of hydraulic cement in the United States for 1902 was 25,753,504 barrels, an increase of 5,684,767 barrels over the quantity produced during the preceding year. The value of this production was \$25,366,380.

Of the entire quantity, 17,230,644 barrels were Portland, valued at \$20,864,078; 8,044,305 barrels were natural-rock, valued at \$4,076,630, and 478,555 barrels were Pozzuolana or slag cement, valued at \$425,672.

The growth of the cement industry is indicated by the fact that, although the increase in production for 1901 over 1900 reached the large number of 2,837,587 barrels, the increase in production for 1902 over 1901 was 5,684,767 barrels. It is of interest here to note that in 1892, just ten years ago, the entire production of cement in the United States was but 8,758,621 barrels, of which 8,211,181 barrels were natural-rock and 547,440 barrels were Portland.

Pennsylvania holds leading place as a producer of Portland cement, while New Jersey follows in second place. The counties of Lehigh and Northampton, Pennsylvania, formerly

included all the factories producing Portland cement in the state; now, although they are still the center of that industry, there are five plants in other counties, none of them, however, ranking at present among the very large producers. Under all other sections is included the production of Alabama, California, Colorado, Georgia, Illinois, Indiana, Kansas, Missouri, South Dakota, Texas, Utah and Virginia.

RELATION OF DOMESTIC PRODUCTION AND CONSUMPTION TO IMPORTS.

The increase, both in the use and in the production of Portland cement in the United States within the last thirteen years, as compared with natural-rock cement and with imported cement, is shown in the following table:

Comparative production of Portland and of natural-rock cement in the United States and of imports of hydraulic cement, 1890-1902.

Year.	Natural cement.	Portland cement.	Total of natural and Port- land ce- ment.	Imports.
	<i>Barrels.</i>	<i>Barrels.</i>	<i>Barrels.</i>	<i>Barrels.</i>
1890.....	7,082,204	385,500	7,417,704	1,940,188
1893.....	7,411,815	590,652	8,002,467	2,674,149
1895.....	7,741,077	990,324	8,731,401	2,997,395
1897.....	8,311,688	2,677,775	10,989,463	2,090,924
1899.....	9,868,179	5,652,266	15,520,445	2,108,388
1900.....	8,383,519	8,482,020	16,865,539	2,386,683
1901.....	7,084,823	12,711,225	19,796,048	939,330
1902.....	8,044,305	17,230,644	25,274,949	1,961,013

This table does not include the production of Pozzuolana or slag cement reported by this bureau for the last three years, which is as follows: 1900, 365,611 barrels; 1901, 272,689 barrels; 1902, 478,555 barrels.

Following is a diagram showing the growth of the domestic production of Portland cement, the increase of total consumption of Portland cement, and the decline of the imports of foreign hydraulic cements during the last thirteen years.

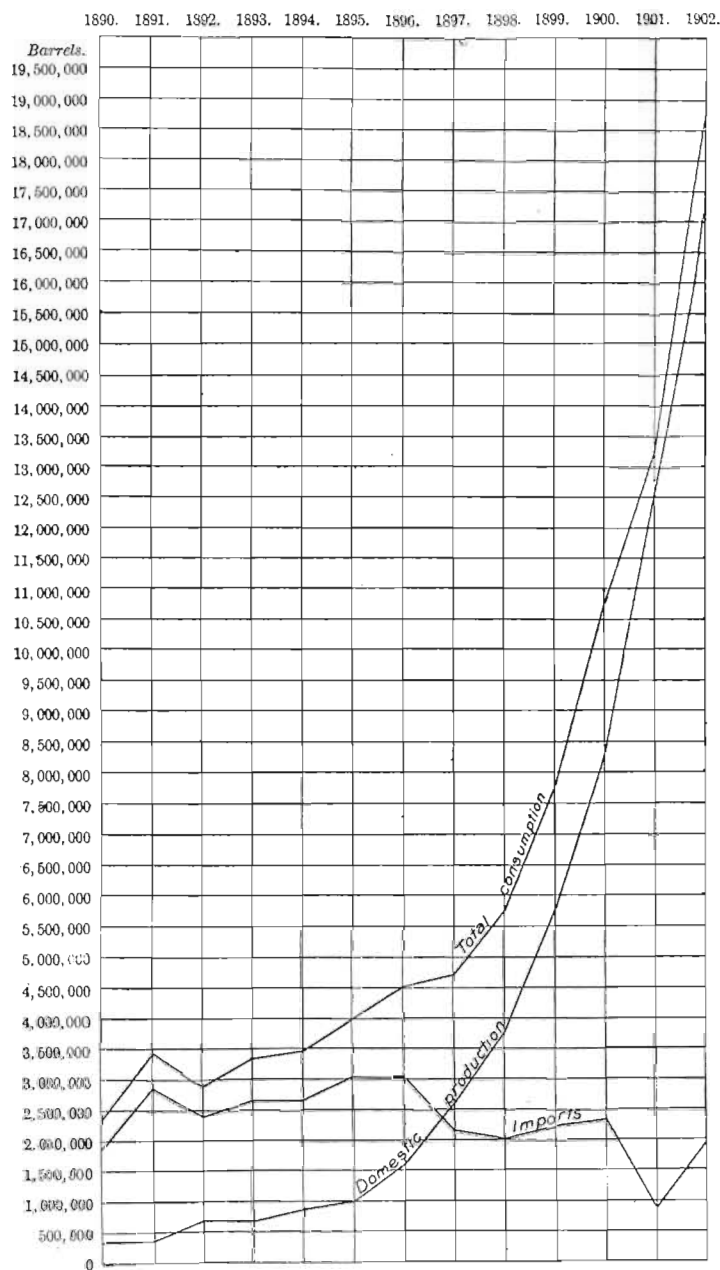


PLATE 2.—Diagram showing the relation of domestic production of Portland cement to imports and to total consumption of Portland cement in the United States, by years and by barrels, from 1890 to 1902, inclusive.

USES OF CEMENT.

The increased use of Portland cement has quite kept pace with its larger production. It is constantly being used in new situations, as well as being substituted for cementing materials. It is now very largely used in the place of lime or other mortars in ordinary wall construction. Immense quantities are used in concrete work for foundations of all kinds and, lately, for concrete, and steel and concrete construction of walls. It is made up into artificial building blocks and is being used experimentally for fence posts and railway ties. In the western states the railways afford the largest market, since culverts and bridge abutments of all kinds are now largely made of it. It has many minor and novel uses.

SCOPE OF THIS REPORT.

The present report is the outgrowth of work taken up by the writer in 1899 and 1900 while serving as Assistant State Geologist of Iowa. At that time material was collected from the most promising localities and a series of analyses and tests were undertaken by Mr. A. E. Lundteigen, who was at that time connected with the Western Portland Cement Company, and later with the Peerless Portland Cement Company. Mr. Lundteigen's results, a portion of which are herewith published, were most encouraging, but the series was not completed, and, pending their completion, it was thought better to make no publication.

In 1903 Mr. E. C. Eckel, of the United States Geological Survey, undertook the preparation for that organization of a special report upon the cement materials of the United States, and it was decided that so far as relates to Iowa the work should be done in co-operation between the Federal and the State Survey. The present report is the result. In this Mr. Eckel discusses the general nature of the materials and processes employed in the manufacture of Portland cement, and the writer gives a brief discussion of the materials available in Iowa. For details as to local geology the reader is referred to the various county reports already published, and for data regarding limes and natural cement rock, he is referred to the

same source. The attempt has been made to indicate somewhat generally the distribution of the materials available, and specifically the nature of these materials. In order that intending manufacturers may have as full a comprehension of the cement industry as possible, Mr. Eckel has discussed not only materials available in Iowa, but those which may be used in competition with any local plant.

THE MATERIALS AND MANUFACTURE OF PORTLAND CEMENT.*

BY EDWIN C. ECKEL.

The Relation of Portland to Other Cements.

It seems desirable, before taking up the specific subject of Portland cement, to indicate the relationships existing between Portland and other cementing materials. These relationships, both as regards resemblances and differences, seem to be best brought out by the classification presented below. This grouping is based primarily upon the amount of chemical change caused by the processes of manufacture and use; and secondarily upon the chemical composition of the cement after setting. As regard is paid to both technologic and commercial considerations, it would seem to be a fairly satisfactory working classification.

GROUP I. SIMPLE CEMENTS.

Simple Cements include all those cementing materials produced by the expulsion of a liquid or gas from the raw material; and whose setting properties are due to the simple reabsorption of the same liquid or gas and the reassumption of the original composition; the set cement being therefore similar in composition to the raw material.

NOTE.—The paper on the raw materials and methods of manufacture of Portland cement has been prepared as the result of field work and other investigations carried on by the writer for the United States Geological Survey. Certain sections of the contribution have appeared, in slightly different form, in "Municipal Engineering" during the past two years.

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Sub-group I a. Hydrate Cements; setting properties due to reabsorption of water.

Sub-group I b. Carbonate Cements; setting properties due to reabsorption of carbon dioxide.

GROUP II. COMPLEX CEMENTS.

Complex cements include all those cementing materials whose setting properties are due to the action of entirely new chemical compounds which were formed during manufacture or use; the set cement being therefore different in composition from the raw material.

Sub-group II a. Silicate Cements; setting properties due largely to the formation of silicates.

Sub-group II b. Oxychloride Cements; setting properties due to the formation of oxychlorides.

GROUP I. SIMPLE CEMENTS.

The cementing materials included in the present group are those known commercially as "plasters," "hard-finishings cements" and "limes."

The material from which the "plasters" and "hard-finishings cements" are derived is gypsum, a hydrous calcium sulphate; while the limes are derived from limestone, which is essentially calcium carbonate, though usually accompanied by greater or less amounts of magnesium carbonate.

On heating gypsum to a certain temperature, the raw material parts readily with much of its water, leaving an almost anhydrous calcium sulphate, known commercially as plaster of Paris. On exposing this plaster to water, it re-hydrates, and again takes the composition of the gypsum from which it was derived.

In like manner limestone, on being sufficiently heated, gives off its carbon dioxide, leaving calcium oxide or "quicklime." This, on exposure to moisture and air carrying carbon dioxide, reabsorbs carbon dioxide and reassumes its original composition, calcium carbonate.

The cementing materials included in this group, therefore, while differing in composition and properties, agree in certain important points. They are all manufactured by heating a

natural raw material sufficiently to remove much or all of its water or carbon dioxide; and, in all, the setting properties of the cementing material are due to the fact that, on exposure to the water or carbon dioxide which has thus been driven off, the cement reabsorbs the previously expelled liquid or gas, and re-assumes the chemical composition of the raw material from which it was derived.

Plaster of Paris, after setting, is not chemically different from the gypsum from which it was derived; while if the sand, added to avoid shrinkage, be disregarded, hardened lime mortar is nothing more or less than an artificial limestone.

SUB-GROUP I a. HYDRATE CEMENTS.

The materials here included are known in commerce as "plaster of Paris," "Cement plaster," "Keene's cement," "Parian cement," etc. All of these hydrate cements are based upon one raw material, gypsum. The partial dehydration of pure gypsum produces plaster of Paris. By the addition to gypsum, either by nature or during manufacture, of relatively small amounts of other materials; or by slight variations in the processes of manufacture, the time of setting, hardness, and other important technical properties of the resulting plaster can be changed to a sufficient degree to warrant separate naming and descriptions of the products.

Both the technology and the chemistry of the processes involved in the manufacture of the hydrate cements are simple. The mineral gypsum, when pure, is a hydrous sulphate of lime, of the formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, corresponding to the composition calcium sulphate 79.1 per cent, water 20.9 per cent. As noted later (under the head of Cement Plasters) gypsum, as mined, rarely even approximates to this ideal composition, its impurities often amounting to 25 per cent or even more. These impurities, chiefly clayey materials and fragments of quartz and limestone, often exercise an appreciable effect upon the properties of the plaster resulting from burning such impure gypsum.

SUB-GROUP I b. CARBONATE CEMENTS.

The cementing materials falling in the present sub-group are oxides, derived from natural carbonates by the application of heat. On exposure, under proper conditions, to any source of carbon dioxide, the cementing material recarbonates and "sets." In practice the carbon dioxide required for setting is obtained simply by exposure of the mortar to the air. In consequence the set of these carbonate cements, as commonly used, is very slow (owing to the small amount of carbon dioxide which can be taken up from ordinary air); and, what is more important from an engineering point of view, none of the mortar in the interior of a wall ever acquires hardness, as only the exposed portions have an opportunity to absorb carbon dioxide. From the examination of old mortars it has been thought probable that a certain amount of chemical action takes place between the sand and the lime, resulting in the formation of lime silicates; but this effect is slight and of little engineering importance compared with the hardening which occurs in consequence of the reabsorption of carbon dioxide from the air.

Limestone is the natural raw material whose calcination furnishes the cementing materials of this group. If the limestone be an almost pure calcium carbonate it will, on calcination, yield calcium oxide or "quicklime." If, however, the limestone should contain any appreciable percentage of magnesium carbonate, the product will be a mixture of the oxides of calcium and magnesium, commercially known as magnesian lime. A brief sketch of the mineralogic relationships of the various kinds of limestone, in connection with the chemistry of lime burning will be of service at this point of the discussion.

Pure limestone has the composition of the mineral calcite, whose formula is (CaCO_3) , corresponding to the composition calcium oxide 56 per cent; carbon dioxide, 44 per cent. In the magnesian limestones part of this calcium carbonate is replaced by magnesium carbonate, the resulting rock therefore having a formula of the type $(x \text{ Ca CO}_3), (y \text{ Mg CO}_3)$. This replacement may reach the point at which the rock has the composition of the mineral dolomite, an equal mixture of the two carbonates, with the formula $(\text{Ca CO}_3), (\text{Mg CO}_3)$, corresponding to the composi-

tion calcium oxide, 30.44 per cent; magnesium oxide, 21.74 per cent; carbon dioxide, 44.22 per cent. Limestones may, therefore, occur with any intermediate amount of magnesium carbonate, and the lime which they produce on calcination will carry corresponding percentages of magnesium oxide, from 0 per cent to 21.74 per cent. Commercially those limes which carry less than 10 per cent of magnesium oxide are, for building purposes, marketable as "pure limes", while those carrying more than that percentage will show sufficiently different properties to necessitate being marketed as "magnesian limes."

Aside from the question of magnesia, a limestone may contain a greater or lesser amount of impurities. Of these the most important are silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3). These impurities, if present in sufficient quantity, will materially affect the properties of the lime produced, as will be noted later under the heads of Hydraulic Limes and Natural Cements.

The carbonate cements may be divided into two classes—

- (1) High calcium limes;
- (2) Magnesian limes.

High Calcium Limes.—On heating a relatively pure carbonate of lime to a sufficiently high degree, its carbon dioxide is driven off, leaving calcium oxide (CaO) or "quicklime." Under ordinary conditions, the expulsion of the carbon dioxide is not perfectly effected until a temperature of 925°C . is reached. The process is greatly facilitated by blowing air through the kiln, or by the injection of steam. On treating quicklime with water, "slaking" occurs, heat being given off, and the hydrated calcium oxide (CaH_2O_2) being formed. The hydrated oxide will, upon exposure to the atmosphere, slowly reabsorb sufficient carbon dioxide to reassume its original composition as lime carbonate. As this reabsorption can take place only at points where the mortar is exposed to the air, the material in the middle of thick walls never becomes recarbonated. In order to counteract the shrinkage which would otherwise take place during the drying of the mortar, sand is invariably added in the preparation of lime mortars, and as noted above, it is probable that certain reactions take place between the lime and the

sand. Such reactions, however, though possibly contributing somewhat to the hardness of old mortars, are only incidental and subsidiary to the principal cause of setting, recarbonation. The presence of impurities in the original limestone affects the character and value of the lime produced. Of these impurities, the presence of silica and alumina in sufficient quantities will give hydraulic properties to the resulting limes; such materials will be discussed in the next group as Hydraulic Limes and Natural Cements.

Magnesian Limes.—The presence of any considerable amount of magnesium carbonate in the limestone from which a lime is obtained has a noticeable effect upon the character of the product. If burned at the temperature usual for a pure limestone, magnesian limestones give a lime which slakes slowly without evolving much heat, expands less in slaking, and sets more rapidly than pure lime. To this class belong the well known and much used limes of Canaan (Conn.); Tuckahoe, Pleasantville and Ossining (N. Y.); various localities in New Jersey and Ohio; and Cedar Hollow (Penn.). Magnesian limes are made at a number of points in Iowa, including Dubuque, Lime City, Cedar Valley and other points.* Under certain conditions of burning, pure magnesian limestones yield hydraulic products, but in this case, as in the case of the product obtained by burning pure magnesite, the set seems to be due to the formation of a hydroxide rather than of a carbonate. Magnesian limestones carrying sufficient silica and alumina will give, on burning, a hydraulic cement falling in the next group under the head of Natural Cements.

GROUP II. 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 interac-

*See Houser, G. L., Iowa Geological Survey, Vol. I, pp. 199-207, 1893. Calvin and Bain, Ibid., Vol. X, pp. 601-604, 1900.

tion, 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 degrees); and this property of hydraulicity is, in all, due largely or entirely to the formation of tri-calcic silicate ($3\text{CaO}, \text{SiO}_2$). 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 silico-aluminous 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.

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 ca-

bonate is so low, relatively 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 limes on the one hand, and Portland cement on the other, agreeing with both in the possession of hydraulic properties. They differ from hydraulic limes, 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 limestone, carrying from 13 to 35 per cent of clayey 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 give 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. S., 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 yield 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 magnesian 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 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

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

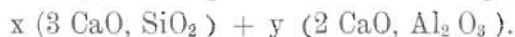
from natural mixtures, without pulverizing and artificially mixing the materials prior to burning. Several plants, however, have placed on the market so-called Portland cements made by grinding up together the underburned and overburned materials formed during the burning of natural cements. Several 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, SiO_2 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 di-calcic aluminate ($2 \text{ CaO}, \text{Al}_2 \text{O}_3$). This would give, as stated by Newberry, for the general formula of a pure Portland—



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 limestones 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 manufacturers prefer to carry it as low as possible. Newberry has stated that in amounts of less than three and one-half 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 purposes 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 (Ca CO_3) and twenty per cent of silica (SiO_2), alumina ($\text{Al}_2 \text{O}_3$) and iron oxide ($\text{Fe}_2 \text{O}_3$) 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 be readily 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 materials are actually used in practice.

In certain localities deposits of argillaceous (clayey) limestone or "cement rock" occurs, 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 furnished 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 silica-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.

ORIGIN AND GENERAL CHARACTERS OF LIMESTONES.

The cement materials which are described in the four following sections as argillaceous limestone or cement rock, pure hard limestone, chalk, and marl, though differing sufficiently in their physical and economic characters to be discussed separately and under different names, agree in that they are all forms of limestone. The origin, chemical composition, physical characters, and properties of limestone will therefore be briefly taken up in the present chapter to serve as an introduction to the more detailed statements concerning the various types of limestone to be found in the succeeding chapters.

ORIGIN OF LIMESTONES.*

Limestones have been formed largely by the accumulation at the sea bottom of the calcareous remains of such organisms as the foraminifera, corals, and mollusks. Most of the thick and extensive limestone deposits of the United States were probably deep-sea deposits formed in this way. Many of these limestones still show the fossils of which they were formed, but in others all trace of organic origin has been destroyed by the fine grinding to which the shells and corals were subjected before their deposition on the sea bottom. It is probable, also, that part of the calcium carbonate of these limestones was a purely chemical deposit from solution, cementing the shell fragments together.

A far less extensive class of limestones—though important in the present connection—owe their origin to the indirect action of organisms. The "marls," so important today as Portland cement materials, fall in this class. As the class is of limited extent, however, its methods of origin may be dismissed here, but will be described later.

Deposition from solution by purely chemical means has undoubtedly given rise to numerous limestone deposits. When

*For a more detailed discussion of this subject the reader will do well to consult Chapter 3 of Prof. J. F. Kemp's "Handbook of Rocks."

this deposition took place in caverns or in the open air, it gave rise to onyx deposits and to the "travertine marls" of certain Ohio and other localities; when it took place in isolated portions of the sea through the evaporation of the sea water it gave rise to the limestone beds which so frequently accompany deposits of salt and gypsum.

VARIETIES OF LIMESTONE.

A number of terms are in general use for the different varieties of limestone, based upon differences of origin, texture, composition, etc. The more important of these terms will be briefly defined.

The *marbles* are limestone which, through the action of heat and pressure, have become more or less distinctly crystalline. The term *marl*, as at present used in cement manufacture, is applied to a loosely cemented mass of lime carbonate formed in lake basins. *Calcareous tufa* and *travertine* are more or less compact limestones deposited by spring or stream waters along their courses. *Oolitic limestones*, so called because of their resemblance to a mass of fish-roe, are made up of small, rounded grains of lime carbonate. *Chalk* is a fine-grained limestone composed of finely comminuted shells, particularly those of the foraminifera. The presence of much silica gives rise to a *siliceous* or *cherty* limestone. If the silica present is in combination with alumina, the resulting limestone will be *clayey* or *argillaceous*.

CHEMICAL COMPOSITION OF LIMESTONE.

A theoretically pure limestone is merely a massive form of the mineral calcite. Such an ideal limestone would therefore consist entirely of calcium carbonate or carbonate of lime, with the formula CaCO_3 (CaO , CO_2), corresponding to the composition calcium oxide (CaO) 56 per cent, carbon dioxide or carbonic acid (CO_2) 44 per cent.

As might be expected, the limestones we have to deal with in practice depart more or less widely from this theoretical composition. These departures from ideal purity may take place along either of two lines:

- a. The presence of magnesia in place of part of the lime.

b. The presence of silica, iron, alumina, alkalis, or other impurities.

It seems advisable to discriminate between these two cases, even though a given sample of limestone, may fall under both heads. and they will, therefore, be discussed separately.

The presence of magnesia in place of part of the lime.—The theoretically pure limestones are, as above noted, composed entirely of calcium carbonate and correspond to the chemical formula CaCO_3 . Setting aside for the moment the question of the presence or absence of such impurities as iron, alumina, silica, etc., it may be said that lime is rarely the only base in a limestone. During or after the formation of the limestone a certain percentage of magnesia is usually introduced in place of a part of the lime, thus giving a more or less magnesian limestone. In the magnesian limestones part of this calcium carbonate is replaced by magnesium carbonate (Mg CO_3), the general formula for a magnesian limestone being therefore



In this formula x may vary from 100 per cent to zero, while y will vary inversely from zero to 100 per cent. In the particular case of this replacement where the two carbonates are united in equal *molecular* proportions, the resultant rock is called dolomite. It has the formula (CaCO_3 , MgCO_3) corresponding to the composition calcium carbonate 54.35 per cent, magnesium carbonate 45.65 per cent. In the case where the calcium carbonate has been entirely replaced by magnesium carbonate, the resulting pure carbonate of magnesia is called magnesite, having the formula MgCO_3 and the composition magnesia (MgO) 47.6 per cent, carbon dioxide (CO_2) 52.4 per cent.

Rocks of this series may therefore vary in composition from pure calcite limestone at one end of the series to pure magnesite at the other. The term limestone has, however, been restricted in general use to that part of the series lying in composition between calcite and dolomite, while all those more uncommon phases carrying more magnesium carbonate than the 45.65 per cent are usually described simply as impure magnesites.

The presence of much magnesia in the finished cement is considered undesirable, $3\frac{1}{2}$ per cent being the maximum permissible under most specifications, and therefore the limestone to be used in Portland cement manufacture should carry not over five to six per cent of magnesium carbonate.

Though magnesia is often described as an "impurity" in limestone, this word, as can be seen from the preceding statements, hardly expresses the facts in the case. The magnesium carbonate present, whatever its amount, simply serves to replace an equivalent amount of calcium carbonate, and the resulting rock, whether little or much magnesia is present, is still a pure carbonate rock. With the impurities to be discussed in later paragraphs, however, this is not the case. Silica, alumina, iron, sulphur, alkalies, etc., when present, are actual impurities, not merely chemical replacements of part of the calcium carbonate.

The presence of silica, iron, alumina, alkalies and other impurities.—Whether a limestone consists of pure calcium carbonate or more or less of magnesium carbonate, it may also contain a greater or less amount of distinct impurities. From the point of view of the cement manufacturer, the more important of these impurities are silica, alumina, iron, alkalies and sulphur, all of which have a marked effect on the value of the limestone as a cement material. These impurities will, therefore, be taken up in the order in which they are named above.

The silica in a limestone may occur either in combination with alumina, as a clayey impurity, or not combined with alumina. As the effect on the value of the limestone would be very different in the two cases they will be taken up separately.

Silica alone.—Silica, when present in a limestone containing no alumina may occur in one of three forms, and the form in which it occurs is of great importance in connection with cement manufacture.

(1) In perhaps its commonest form, silica is present in nodules, masses or beds of flint or chert. Silica occurring in this form will not readily enter into combination with the lime of a cement mixture, and a cherty or flinty limestone is, therefore, almost useless in cement manufacture.

(2) In a few cases, as in the hydraulic limestone of Teil, France, a large amount of silica is present and very little alumina, notwithstanding which the silica readily combines with the lime on burning. It is probable that in such cases the silica is present in the limestone in a very finely divided condition, or possibly as hydrated silica, possibly as the result of chemical precipitation or of organic action. In the majority of cases, however, a highly siliceous limestone will not make a cement on burning unless it contains alumina in addition to the silica.

(3) In the crystalline limestone (marbles) and less commonly in uncrystalline limestones, whatever silica is present may occur as a complex silicate in the form of shreds of mica, hornblende, or other silicate mineral. In this form silica is somewhat intractable in the kiln, and mica and other silicate minerals are therefore to be regarded as inert and useless impurities in a cement rock. These silicates will flux at a lower temperature than pure silica and are thus not so troublesome as flint or chert. They are, however, much less serviceable than if the same amount of silica were present in combination with alumina as a clay.

Silica with Alumina.—Silica and alumina, combined in the form of clay, are common impurities in limestone, and are of special interest to the cement manufacturer. The best known example of such an argillaceous limestone is the cement rock of the Lehigh district of Pennsylvania. Silica and alumina, when present in this combined form, combine readily with the lime under the action of heat, and an argillaceous limestone therefore forms an excellent basis for a Portland cement mixture.

Iron.—Iron when present in a limestone occurs commonly as the oxide (Fe_2O_3) or sulphide (FeS_2); more rarely as iron carbonate or in a complex silicate. Iron in the oxide, carbonate or silicate forms is a useful flux, aiding in the combination of the lime and silica in the kiln. When present as a sulphide, in the form of the mineral pyrite, it is to be avoided in quantities above two or three per cent.

PHYSICAL CHARACTERS OF LIMESTONES.

In texture, hardness and compactness, the limestones vary from the loosely consolidated marls through the chalks to the hard, compact limestones and marbles. Parallel with these variations are variations in absorptive properties and density. The chalky limestones may run as low in specific gravity as 1.85, corresponding to a weight of about 110 pounds per cubic foot, while the compact limestones commonly used for building purposes range in specific gravity between 2.3 and 2.9, corresponding approximately to a range in weight of from 140 to 185 pounds per cubic foot.

From the point of view of the Portland cement manufacturer, these variations in physical properties are of economic interest chiefly in their bearing upon two points: the percentage of water carried by the limestone as quarried, and the ease with which the rock may be crushed and pulverized. To some extent the two properties counterbalance each other, the softer the limestone the more absorbent it is likely to be. These purely economic features will be discussed in more detail later.

EFFECT OF HEATING ON LIMESTONE.

On heating a non-magnesian limestone to or above 300° C., its carbon dioxide will be driven off, leaving quicklime (calcium oxide, CaO). If a magnesian limestone be similarly treated, the product would be a mixture of calcium oxide and magnesium oxide (MgO). The rapidity and perfection of this decomposition can be increased by passing steam or air through the burning mass. In practice this is accomplished either by the direct injection of air or steam, or more simply by thoroughly wetting the limestone before putting it into the kiln.

If, however, the limestone contains an appreciable amount of silica, alumina and iron, the effects of heat will not be of so simple a character. At temperatures of 800° C. and above these clay impurities will combine with the lime oxide, giving silicates, aluminates and related salts of lime. In this manner a natural cement will be produced. An artificial mixture of certain and uniform composition, burned at a higher tempera-

ture, will give a Portland cement, the details of whose manufacture are discussed on later pages.

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. As this area still furnishes about two-thirds of all the Portland cement manufactured in the United States, its raw materials will be described in some detail.

CEMENT ROCK OF THE LEHIGH DISTRICT.

The Lehigh district of the cement trade comprises parts of Berks, Lehigh, and Northampton counties, Pennsylvania, and of Warren county, New Jersey. Within this relatively small area about twenty Portland cement mills are located, producing slightly over two-thirds of the entire American output. As deposits of the cement rock used by these plants extend far beyond the present "Lehigh district," a marked extension of the district will probably take place as the need for larger supplies of raw material becomes more apparent.

The "cement rock" of the Lehigh district is a highly argillaceous limestone of Trenton (Lower Silurian) age. The formation is about 300 feet in thickness in this area. The rock

is very dark gray in color and usually has a slaty fracture. In composition it ranges from about 60 per cent lime carbonate with 30 per cent clayey material, up to about 80 per cent lime carbonate with 15 per cent of silica, alumina and iron. The lower beds of the formation are always higher in lime carbonate than are the beds nearer the top of the formation. The content of magnesium carbonate in these cement rocks is always high (as Portland cement materials go), ranging from 3 to 6 per cent.

Near, and in some cases immediately underlying these cement beds, are beds of purer limestone ranging from 85 to 96 per cent lime carbonate. The usual practice in the Pennsylvania and New Jersey plants has been, therefore, to mix a relatively small amount of this purer limestone with the low lime "cement rock" in such proportions as to give a cement mixture of proper composition.

The economic and technologic advantages of using such a combination of materials are very evident. Both the pure limestone and the cement rock, particularly the latter, can be quarried very easily and cheaply. As quarried, they carry but little water so that the expense of drying them is slight. The fact that about four-fifths of the cement mixture will be made up of a natural cement rock permits coarser grinding of the raw mixture than would be permissible in plants using pure limestone or marl with clay. This point is more fully explained on a later page. It seems probable, also, that when using a natural cement rock as part of the mixture the amount of fuel necessary to clinker the mixture is less than when pure limestone is mixed with clay.

Such mixtures of argillaceous limestone or "cement rock" with a small amount of pure limestone evidently possess important advantages over mixtures of pure hard limestone or marl with clay. They are, on the other hand, less advantageous as cement materials than the chalky limestones.

The analyses in table 2 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.

TABLE 2. ANALYSES OF LEHIGH DISTRICT CEMENT MATERIALS.

	Cement Rock.				Limestone.	
Silica (SiO_2)	10.02	9.52	14.52	16.10	3.02	1.98
Alumina (Al_2O_3)	6.26	4.72	6.52	2.20	1.90	0.70
Iron oxide (Fe_2O_3)
Lime carbonate (CaCO_3)	78.65	80.71	73.52	76.23	92.05	95.19
Magnesium carbonate (MgCO_3)	4.71	4.92	4.69	3.54	3.04	2.03

"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 table 3.

TABLE 3. ANALYSES OF "CEMENT ROCK" MATERIALS FROM THE WESTERN UNITED STATES.

	Utah.		California.		Colorado.	
	Cement rock.	Limestone.	Cement rock.	Limestone.	Cement rock.	Limestone.
Silica (SiO_2)	21.2	6.8	20.06	7.12	14.20
Alumina (Al_2O_3)	8.0	3.0	10.07	2.36	5.21
Iron oxide (Fe_2O_3)	3.39	1.16	1.73
Lime carbonate (CaCO_3)	62.08	89.8	63.40	87.70	75.10	88.0
Magnesium carbonate (MgCO_3)	3.8	0.76	1.54	0.84	1.10

In addition to the "cement rocks" noted in this chapter, it is necessary to call attention to the fact that many of the chalky limestones are sufficiently argillaceous to be classed as "cement rocks." Because of their softness, however, all the chalky limestones will be described together.

PURE HARD LIMESTONES.

Soon after the American Portland cement industry had become fairly well established in the Lehigh district, attempts were made in New York state to manufacture Portland cement from a mixture of pure limestone and clay. These attempts were not commercially successful, and although their lack of succes-

was not due to any defects in the limestone used, a certain prejudice arose against the use of the hard limestones. In recent years, however, this has disappeared, and a very large proportion of the American output is now made from mixtures of limestone with clay or shale. This reestablishment in favor of the hard limestone is doubtless due, in great part, to recent improvements in grinding machinery, for the purer limestones are usually much harder than argillaceous limestones like the Lehigh district "cement rock," and it was very difficult to pulverize them finely and cheaply with the crushing appliances in use when the Portland cement industry was first started in America.

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.

ANALYSES OF PURE HARD LIMESTONES AND CLAYEY MATERIALS.

Limestones				
Silica (SiO_2)	1.72	0.86	0.56	0.40
Alumina (Al_2O_3).....	1.63	0.63	1.23	0.44
Iron oxide (Fe_2O_3).....	6.59	1.03	0.29	
Lime carbonate (CaCO_3).....	90.58	97.06	97.23	97.99
Magnesium carbonate (MgCO_3).....			0.75	0.42
Clays and Shales.				
Silica (SiO_2).....	63.56	55.80	56.30	60.00
Alumina (Al_2O_3).....	27.32	30.20	29.86	23.26
Iron oxide (Fe_2O_3).....				4.32
Lime carbonate (CaCO_3).....	3.60	2.54		1.70
Magnesium carbonate (MgCO_3).....	2.60			1.50

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 high-silica 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 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.

GEOGRAPHIC AND GEOLOGIC DISTRIBUTION IN THE UNITED STATES.

The chalks and chalky limestones are confined almost entirely to certain southern and western states. They are all of approximately the same geologic ages, Cretaceous or Tertiary, and are mostly confined to one division of the Cretaceous. The principal chalk or soft limestone deposits available for use in Portland cement manufacture occur in three widely separated areas, occupying respectively, (a) parts of Alabama and Mississippi, (b) parts of Texas and Arkansas, (c) parts of Iowa, Nebraska, North and South Dakota.

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 table C, and will serve to show their range of composition.

TABLE C. CHALKY LIMESTONES.

	Demopolis, Ala.	San Antonio, Tex.	Dallas, Tex.	White Cliffs, Ark.	Yankton, S. Dak.	Milton, N. Dak.
Silica	12.13	5.77	23.55	7.97	8.20	9.15
Alumina	4.17	2.14	1.50	1.09	7.07	4.80
Iron oxide, °	3.28					
Lime carbonate	75.07	90.15	70.21	88.64	83.59	63.75
Magnesian carbonate92	.58	.58	.73	n. d.	1.25

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 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.

A warning to the reader concerning other uses of the term "marl," may profitably be introduced here. The meaning above given is that in which the term marl is commonly used in the cement industry at the present day but in geological and agricultural reports, particularly in those issued before the Portland cement industry became prominent in this country, the term marl has been used to cover several very different substances. The following three uses of the term will be found particularly common, and must be guarded against when such reports are being examined in search for descriptions of deposits of cement materials.

(1) In early days the terms "marls" and "marlytes" were used to describe deposits of calcareous shales, and often covered

shales which were not particularly calcareous. This use of the term will be found in many of the earlier geological reports issued by New York, Ohio, and other interior states.

(2) In New Jersey and the states southward bordering on the Atlantic and the Gulf of Mexico, the term marl is commonly applied to deposits of soft, chalky or unconsolidated limestone, often containing considerable clayey and phosphatic matter. These limestones are of marine origin, and are not related to the fresh water marl deposits which are the subject of the present chapter.

(3) In the same states as are included in the last paragraph, but particularly in New Jersey and Virginia, large deposits of the so-called "greensand marls" occur. This material is in no way related to the true marls (which are essentially lime carbonates), but consists almost entirely of an iron silicate, with very small percentages of clayey, calcareous and phosphatic matter.

ORIGIN OF MARLS.

The exact cause of the deposition of marls has been the subject of much investigation and discussion, particularly in the past few years, since they have become of economic importance. The reader who wishes to obtain further details concerning this question will do well to refer to the following series of papers.

(1) Blatchley, W. S., and Ashley, G. H. The lakes of northern Indiana and their associated marl deposits, in 25th Ann. Rept. Indiana Dept. Geology and Natural Resources, pp. 31-321.

(2) Davis, C. A. A contribution to the natural history of marl. Journal of Geology, Vol. 8, pp. 485-497.

(3) Davis, C. A. Second contribution to the natural history of marl. Journal of Geology, Vol. 9, pp. 491-506.

(4) Davis, C. A. A contribution to the natural history of marl. Vol. 8, pt. 3. Reports Michigan Geological Survey, pp. 65-102.

(5) Lane, A. C. Notes on the origin of Michigan bog limes, Vol. 8, pt. 3, Reports Michigan Geological Survey, pp. 199-223.

Disregarding the points in controversy, which are of no particular practical importance, it may be said that marls are deposited in lakes by spring or stream waters carrying lime car-

bonate in solution. The actual deposition is in part due to purely physical and chemical causes, and in part to the direct or indirect action of animal or vegetable life. The result, in any case, is that a calcareous deposit forms along the sides and over the bottom of the lake, this deposit consisting of lime carbonate, mostly in a finely granular form, interspersed with shells and shell fragments.

GEOGRAPHIC DISTRIBUTION OF MARL DEPOSITS

The geographic distribution of marl deposits is intimately related to the geologic history of the region in which they occur. Marl beds are, as indicated in the preceding section, the result of the filling of lake basins. Lakes are not common except in those portions of the United States which were affected by glacial action, since lakes are in general due to the damming of streams by glacial material. Workable marl deposits, therefore, are almost exclusively confined to those portions of the United States and Canada lying north of the former southern limit of the glaciers.

Marl beds are found in the New England states where they are occasionally of important size, and in New York, where large beds occur in the central and western portions of the state. Deposits are frequent and important in Michigan and in the northern portions of Ohio, Indiana and Illinois. Marl beds occur in Wisconsin and Minnesota, but have not been as yet exploited for cement manufacture.

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:

ANALYSES OF MARLS AND CLAYS USED IN CEMENT PLANTS.

	Marl.			Clay.		
Silica	0.25	3.0	1.60	40.48	52.0	63.75
Alumina.....	.10	1.55	20.95	17.0	16.40
Iron oxide.....					5.0	6.35
Lime carbonate	94.39	93.0	88.9	25.80	20.0	4.0
Magnesium carbonate38	1.5	.94	99	2.1

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:

ANALYSES OF ALKALI WASTE.

	1	2	3	4
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).....			1.38	
Lime (CaO).....	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	0.50
Sulphur trioxide (SO_3).....	n. d.	n. d.	1.26	n. d.
Sulphur (S).....	n. d.	0.10	n. d.	0.06
Carbon dioxide (CO_2).....	42.43	41.70	39.60	n. d.
Water and organic matter.....	n. d.		3.80	n. d.

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 the slag (or puzzolan) cements described on later pages of this report 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_2O_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 are at present engaged in the manufacture of true Portland cement from slag, in the United States.

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)	30.	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 $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 = \frac{\text{SiO}_2}{3}$ is approached.

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.

COMPOSITION OF AMERICAN ROOFING SLATES.

	Maximum	Average.	Minimum.
Silica (SiO_2).....	68.62	60.64	54.05
Alumina (Al_2O_3).....	24.71	18.05	9.77
Iron oxides (FeO , Fe_2O_3).....	10.65	6.87	2.18
Lime (CaO).....	5.23	1.54
Magnesia (MgO).....	6.43	2.60	0.12
Alkalies (K_2O , Na_2O).....	8.68	4.74	1.93
Ferrous sulphide (FeS_2).....	0.38
Carbon dioxide (CO_2).....	1.47
Water of combination..	3.51
Moisture, below 110°C	0.62

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 marls 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 to cars or carts. In a few limestone quarries a steam shovel is employed to do the loading, and in shale quarries this use of steam shovels 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 $33\frac{1}{3}$ 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 lime 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 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 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 marls 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

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

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 limey 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 the 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.

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 112 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 cement 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 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 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 the 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 Pennsylvania cement plants. A mechanical analysis of it showed the following results:

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

†Journ. Amer. Chem. Soc., vol. 25, p. 1106.

	Mesh of Sieve.		
	50	100	200
Per cent passing	96.9	85.6	72.4
Per cent residue	3.1	14.4	27.6

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

GRINDING AND MIXING SLAG-LIMESTONE MIXTURES.

While the manufacture of Portland cement from a mixture of slag and limestone is similar in general theory and practice to its manufacture from a limestone-clay mixture, certain interesting differences occur in the preparation of the mixture. In the following paragraphs the general methods of preparing mixtures of slag and limestone for use in Portland cement manufacture will first be noted, after which certain processes peculiar to the use of this particular mixture will be described separately.

General methods.—After it had been determined that the pozzuolanic cement made* by mixing slag with lime without subsequent burning of the mixture, was not an entirely satisfactory structural material, attention was soon directed toward the problem of making a true Portland cement from such a slag. The blast-furnace slags commonly available, while carrying enough silica and alumina for a cement mixture, are too low in lime to be suitable for Portland cement. Additional lime must be added, usually in the form of limestone, the slag and limestone must be well mixed and the mixture properly burned. The general methods for accomplishing the proper mixture of the materials vary in details. It seems probable that the first method used in attempting to make a true Portland cement from slag, was to dump the proper proportion of limestone, broken into small lumps, into molten slag. The idea was that both mixing and calcination could thus be accomplished in one stage; but in practice it was found that the resulting cement was variable in composition and always low

* See *Municipal Engineering*, vol. 24, p. 335, May, 1903.

in grade. This method has accordingly fallen into disuse, and at present three different general processes of preparing the mixture are practiced at different European and American plants.

(1) The slag is granulated, dried, and ground, while the limestone is dried and ground separately. The two materials are then mixed in proper proportions, the mixture is finely pulverized in tube mills, and the product is fed in a powdered state to rotary kilns.

(2) The slag is granulated, dried, and mixed with slightly less than the calculated proper amount of limestone, which has been previously dried and powdered. To this mixture is added sufficient powdered slaked lime (about 2 to 6 per cent) to bring the mixture up to the correct composition. The intimate mixture and final reduction are then accomplished in ball and tube mills. About 8 per cent of water is then added, and the slurry is made into bricks, which are dried and burned in a dome or chamber kiln.

(3) Slag is granulated and mixed, while still wet, with crushed limestone in proper proportions. This mixture is run through a rotary calciner, heated by waste kiln gases, in which the temperature is sufficient not only to dry the mixture, but also to partly powder it, and to reduce most of the limestone to quicklime. The mixture is then pulverized and fed into rotary kilns.

Of the three general processes above described the second is unsuited to American conditions. The first and third are adapted to the use of the rotary kiln. The third seems to be the most economical, and has given remarkably low fuel consumption in practice, but so far has not been taken up in the United States.

Certain points of manufacture peculiar to the use of mixtures of slag and limestone will now be described.

Composition of the slag.—The slags available for use in Portland cement manufacture are of quite common occurrence in iron-producing districts. Those best suited for such use are the more basic blast-furnace slags, and the higher such slags run in lime the more available they are for this use. The slags utilized will generally run from 30 to 40 per cent lime.

The presence of more than 3 per cent or so of magnesia in a slag is of course enough to render its use as a Portland cement material inadvisable; and on this account slags from furnaces using dolomite (magnesian limestone) as a flux, are unsuited for cement manufacture. The presence of any notable percentage of sulphur is also a drawback, though, as will be later noted, part of the sulphur in the slag will be removed during the processes of manufacture.

Granulation of slag.—If slag be allowed to cool slowly it solidifies into a dense, tough material, which is not readily reduced to the requisite fineness for a cement mixture. If it be cooled suddenly, however, as by bringing the stream of molten slag into contact with cold water, the slag is “granulated,” i. e., it breaks up into small porous particles. This granulated slag or “slag sand” is much more readily pulverized than a slowly cooled slag; its sudden cooling has also intensified the chemical activity of its constituents so as to give it hydraulic properties, while part of the sulphur contained in the original slag has been removed. The sole disadvantage of the process of granulating slag is that the product contains 20 to 40 per cent of water, which must be driven off before the granulated slag is sent to the grinding machinery.

In practice the granulation of the slag is effected by directing the stream of molten slag direct from the furnace into a sheet-iron trough. A small stream of water flows along this trough, the quantity and rate of flow of water being regulated so as to give complete granulation of the slag without using an excessive amount of water. The trough may be so directed as to discharge the granulated slag into tanks or into box cars, which are usually perforated at intervals along the sides so as to allow part of the water to drain off.

Drying the slag.—As above noted, the granulated slag may carry from 20 to 40 per cent of water. This is removed by treating the slag in rotary driers. In practice such driers give an evaporation of eight to ten pounds of water per pound of coal. The practice of slag drying is very fully described in Vol. 10 of the Mineral Industry, pages 84-95, where figures and descriptions of various driers are also given, with data on their evapo-

rative efficiency. As noted earlier in this article, one of the methods of manufacturing Portland cement from slags puts off the drying of the slag until after it has been mixed with the limestone, and then accomplishes the drying by utilizing waste heat from the kilns. Kiln gases could of course be used anyway in the slag driers, but it so happens that they have not been so used except in plants following the method in question.

Grinding the slag.—Slag can be crushed with considerable ease to about 50-mesh, but notwithstanding its apparent brittleness it is difficult to grind it finer. Until the introduction of the tube mill it was almost impossible to reduce this material to the fineness necessary for a cement mixture, and the proper grinding of the slag is still an expensive part of the process as compared with the grinding of limestone, shales or clay.

Composition of the limestone.—As the slag carries all the silica and alumina necessary for the cement mixture, the limestone to be added to it should be simply a pure lime carbonate. The limestone used for flux at the furnace which supplies the slag will usually be found to be of suitable composition for use in making up the cement mixture.

ECONOMICS OF USING SLAG-LIMESTONE MIXTURES.

The manufacture of a true Portland cement from a mixture of slag and limestone presents certain undoubted advantages over the use of any other raw materials, while it has also a few disadvantages.

Probably the most prominent of the advantages lies in the fact that the most important raw material—the slag—can usually be obtained more cheaply than an equal amount of natural raw material could be quarried or mined. The slag is a waste product, and a troublesome material to dispose of, for which reasons it is obtained at small expense to the cement plant. Another advantage is due to the occurrence of the lime in the slag as oxide, and not as carbonate. The heat necessary to drive off the carbon dioxide from an equivalent mass of limestone is therefore saved when slag forms part of

the cement mixture, and very low consumption is obtained when slag-limestone mixture is burned.

Of the disadvantages, the toughness of the slag and the necessity for drying it before grinding are probably the most important. These serve to partly counterbalance the advantages noted above. A third difficulty, which is not always apparent at first, is that of securing a proper supply of suitable slag. Unless the cement plant is closely connected in ownership with the furnaces from which its slag supply is to be obtained, this difficulty may become very serious. In a season when a good iron market exists the furnace manager will naturally give little thought to the question of supplying slag to an independent cement plant.

The advantages of the mixture, however, seem to outweigh its disadvantages, for the manufacture of Portland cement from slag is now a large and growing industry in both Europe and America. Two Portland cement plants using slag and limestone as raw materials have been established for some time in this country, several others are in course of construction at present, and it seems probable that in the near future Alabama will join Illinois and Pennsylvania as an important producer of Portland cement from slag.

GRINDING AND MIXING.—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 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 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 noted in an earlier paper. 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 bad 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. This point will, however, be further discussed in the next article of this series.

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 plant the marl and clay are obtained from a swamp about three-fourths of a mile from the mill. A revolving derrick with clam-shell bucket was employed for excavating the marl, while the clay was dug with shovels. The materials are taken to the works over a private narrow-gage road, on cars carrying about three tons each, drawn by a small locomotive. At the mill the cars were hauled 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 thirty-six 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.

ANALYSES OF CEMENT MIXTURES.

	1	2	3	4
Silica	12.62	13.46	13.85	14.77
Alumina and iron oxide	6.00	?	7.20	4.35
Carbonate of lime	75.46	73.66	73.93	76.84
Magnesium oxide	2.65	?	?	1.74

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.

*Duryee, E., The first manufacture of Portland cement by the direct rotary kiln process. *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, in the *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, 1899.

Stanger, W. H., and Blount, B., The rotary process of cement manufacture. *Proc. Institution Civil Engineers*, Vol. 145, pp. 44-136, 1901.

Editorial, The influence of the rotary kiln on the development of Portland cement manufacture in America. *Engineering News*, May 3, 1900.

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 of simply 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 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 about six feet in diameter; its length, for dry materials, has usually been sixty feet, but during the past year many eighty-foot kilns have been built, while for wet mixtures an eighty-foot, or even longer, kiln is 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 cylinder is set, gradually carries the cement mixture to the lower end of the

*Stanger, W. H., and Blount, B., Gilbert, W., and Candlot, E. (Discussion of the value, design and results obtained from various types of fixed kilns.) Proc. Institution Civil Engineers, Vol. 145, pp. 44, 43, 81, 82, 99, 100. 1901.

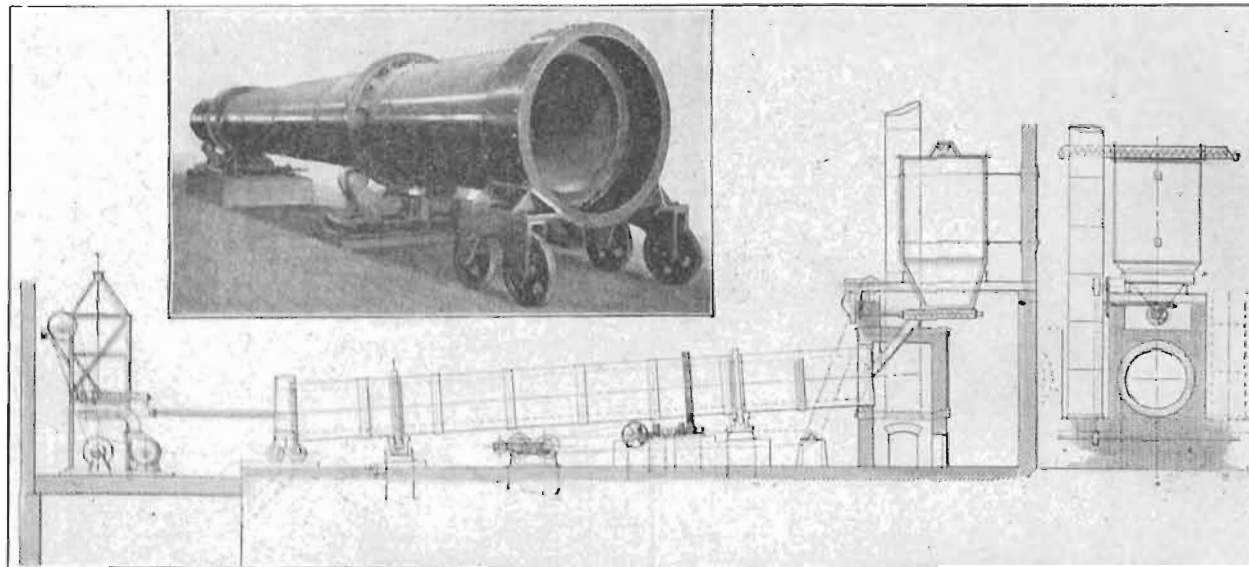


PLATE III. View of the Rotary Kiln, also showing method of firing with powdered coal under blast.

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 $25\frac{1}{2}$ 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 range 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 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 kiln 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 little 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, to 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 a 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 lime 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. Russell gives the following analyses of West Virginia and Pennsylvania coals used at present at various cement plants in Michigan.

ANALYSES OF KILN COALS.

	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.....	6.36	7.06	3.81	6.13
Moisture.....	2.08	1.35	1.00	1.40
Sulphur.....	1.30	1.34	0.42	1.46

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. Usually 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 almost 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 counterbalanced 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 of gypsum 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.

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 $3\text{CaO}, \text{SiO}_2$,—tricalcic silicate. To this compound is 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 $3\text{CaO}, \text{SiO}_2$. 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 $3\text{CaO}, \text{SiO}_2$) 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. This point will be further discussed in later pages.

It is generally considered that whatever alumina is present in the cement is combined with part of the lime to form the compound $2\text{CaO}, \text{Al}_2\text{O}_3$,—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 $2\text{CaO}, \text{Fe}_2\text{O}_3$. For the purposes of the present paper it will be sufficient to say that, in the relatively small percentages in which iron occurs in Portland cement, it may for convenience be considered as entirely equivalent to alumina

and its action, and the two may be calculated together. When alumina is named in this paper, therefore, it will be understood to include any iron that may be present.

CEMENT MATERIALS IN IOWA.

BY H. FOSTER BAIN.

General Statement.

Materials capable of furnishing the silica and alumina necessary to the manufacture of Portland cement are widespread, and the location of new plants is apt to be determined by the presence of suitable calcareous deposits and favorable industrial conditions. Iowa affords no exception to these general rules. In practically all parts of the state there are shales or clays which might if necessary be used as one of the constituents of a cement mixture. The indurated rocks from the Ordovician to the Cretaceous afford shales of wide distribution and excellent character. The surface formations supplement these resources with loess, alluvium, and certain minor bodies of water-laid clay of glacial derivation. The shales and the clays have been extensively studied and a special report upon them by Dr. S. W. Beyer was published in 1904. For present purposes it will suffice to say that such material suitable for use in the manufacture of Portland cement can be found at almost every point in the state where other conditions are favorable to its production.

The calcareous constituent of cements is most commonly derived from marls, chalk and limestone. All these occur within the state though they are of very unequal importance.

CALCAREOUS MARLS.

Marls are extensively used at several points in the United States in the manufacture of cement. The large cement in-

dustry of Michigan in particular is founded upon the occurrence within that state of extensive deposits of calcareous marl in the shallow lakes of the lower peninsula*. Similar marls are used in New Jersey and Ohio. The lakes in which the marl occurs are located within the area covered by the Wisconsin drift, and similar lakes are particularly characteristic of such areas. In Iowa the north central portion of the state is covered by drift of Wisconsin age† and is dotted with small shallow lakes resembling in appearance and genesis those of Michigan. From time to time small amounts of marl have been reported from this area and while so far no bodies of commercial importance have been located it is not impossible that such may be found.

CHALK DEPOSITS.

The Cretaceous deposits which cover the western third of Iowa include important bodies of chalk. With but two exceptions, both of which are unimportant, outcrops of the chalk beds are confined to the valley of the Big Sioux river between Sioux City and Hawarden. The chalk beds received some attention in the course of the early geological surveys of the region and have been recently restudied by Calvin, ‡ Bain § and Wilder ||.

The chalk forms prominent bluffs at intervals and may be well seen near Westfield, Akron and Hawarden. It was referred to the Niobrara formation until Wilder discovered fossils characteristic of the Benton in the shale above. This proves it to be the equivalent of the "Oyster Shell Rim" of the Black Hills or the Graneros limestone. A thickness of twenty to thirty feet is ordinarily seen in individual exposures, but a total thickness of fifty feet is probably present. A generalized section may be given as follows:

* Russell, I. C., Portland Cement Industry in Michigan, 22nd Ann. Rept. U. S. Geol. Surv., pt. III, pp. 635-685.

† See Plate II, Iowa Geol. Surv., Vol. XI, 1900.

‡ Calvin, S., Cretaceous Deposits of Woodbury and Plymouth Counties, etc., Iowa Geol. Surv., Vol. I, pp. 147-161, 1893.

§ Bain, H. F., Cretaceous Deposits of the Sioux Valley, Iowa Geol. Surv., Vol. III, pp. 101-114, 1895; Geology of Woodbury County, Ibid, Vol. V., pp. 273-275, 295-296, 1896; Geology of Plymouth County, Ibid, Vol. VIII, pp. 354-360, 1898.

|| Wilder, F. A., Geology of Lyon and Sioux Counties, Iowa Geol. Surv., Vol. X, pp. 111-115, 151-152 1900.

Section of Chalk Beds.

	FEET.
3. Chalk.....	4 to 6
2. Limestone, soft, splitting into thin slabs and crowded with shells of <i>Inoceramus</i>	12
1. Chalk.....	12

The interbanding of thin bedded limestone and the chalk is quite characteristic. Both materials are soft and grind easily. Almost no magnesia is present, as is shown by the following analyses, and in some instances the chalk beds themselves carry enough or more than enough clay to make a good cement mixture. In all cases excellent clays occur immediately above or below. The clays are now being used at Sioux City and elsewhere in the manufacture of a wide variety of clay products.

Analyses of Iowa Chalks.

	I	II	III
Silica and insol. mat.....	22.70
Iron and alumina (oxides).....	6.68
Calcium carbonate.....	64.30	83.70	94.39
Magnesium carbonate.....	5.38	2.48	.70
Water.....08	.06

- I. Chalk rock, Hawarden, Iowa.....Newberry Anal.
 II. Chalk rock, Westfield, Iowa.....Weems Anal.
 III. Chalk rock, Le Mars, Iowa.....Weems. Anal.

It is evident that materials suitable for the manufacture of Portland cement are available, and this conclusion is confirmed by the fact that at Yankton, S. D., a plant has for many years been in operation in which similar beds, belonging to the Niobrara, are used. Furthermore, in tests carried on at Sioux City cement has been made experimentally from the local material.*

LIMESTONES.

General statement.—Non-magnesian limestones are found in Iowa in the Ordovician, Devonian, and Carboniferous. The

*Lonsdale, E. H., Proc. Iowa Acad. Sci., Vol. II, p. 173, 1895.

limestones of the Cambrian and Silurian are without important exception highly magnesian. Those of the Ordovician are predominantly magnesian, though an exception occurs in the case of the beds which it has been customary to map and discuss under the name Trenton. In eastern Iowa the dolomites and magnesian limestones have heretofore attracted more attention than the non-magnesian rocks, and flourishing lime and building stone industries have been founded upon them. Limestone of one class or the other occurs in all of the eastern and most of the southern counties. In the northwest the covering of Cretaceous and Pleistocene deposits limits the outcrops to a few deep stream valleys. The general distribution of the geological formations of the state is shown in plate II of volume XIV of the present series of reports. For details of localities the reader is referred to the various county reports of the Iowa Geological Survey cited in this text. The transportation facilities available at each point may be best learned from the large map of the state published and distributed gratuitously by the Railway Commissioners.

ORDOVICIAN LIMESTONES.

Below the Devonian there is but one limestone outcropping in Iowa which is at all suitable for Portland cement manufacture. It is known as the Trenton, and occupies portions of Dubuque, Clayton, Fayette, Winneshiek and Allamakee counties.* Under this name have been included and mapped an aggregate of non-magnesian limestones and thin shales, varying in thickness from fifteen to three hundred and fifty feet. The variation in thickness is an expression of the fact that the difference between the Galena and Trenton is lithologic and not formational. It is probable that in the future the division will be made upon some other basis, but for present purposes the lithologic difference is the important one. The strata included on this basis within the Trenton are in the main either non-magnesian or only slightly magnesian. In composition as in geologic position they are almost exactly equivalent to the

* Reports on the geology of Fayette, Winneshiek and Clayton counties are now in preparation. For the geology of Allamakee county, see Iowa Geol. Surv., Vol. IV, pp. 35-120; for Dubuque county, see *Ibid.*, Vol. X, pp. 379-651.

famous cement rock of the Lehigh Valley, from which 60 per cent of the Portland cement production of the United States now comes.

Excellent exposures of the Trenton occur along the Mississippi river and its tributaries in the counties named above. At Specht Ferry, in Dubuque county, the following section was observed.

Specht Ferry Section.

	FEET.
13. Thin-bedded, brown dolomite, with shaly partings (Galena)	4
12. Thin-bedded, imperfectly dolomitized limestone, with fossil brachiopod shells only slightly changed; the limestone brown, earthy, non-crystalline, but evidently of the Galena type.	3
11. Thick, earthy, imperfectly dolomitized beds (Galena)	3
10. Thin limestone beds with much shale in the partings; in part a true shale	5
9. Limestone, bluish, rather coarse-grained, with few fossils.....	4
8. Limestone similar to above	3
7. Limestone similar to above	18
6. Shale, bluish or greenish, containing occasional thin beds or discontinuous flakes of limestone; the "Green Shales" of Minnesota geologists.	12
5. Thin-bedded, bluish, rather coarse-grained limestone, weathering brownish in color.....	5
4. Limestone, in rather heavy layers which range up to fifteen inches in thickness; bluish on fresh fracture, but weathering to buff on exposure.....	5
3. Brittle, fine-grained, blue limestone, very fossiliferous, breaking up on weathered surfaces into flexuous layers about two inches in thickness.....	20
2. Lower buff beds, exposed, about	8
1. Unexposed to level of water in river.....	45

The "Green Shale" No. 6, of the above section, and the limestones above and below were sampled and analyzed by Mr. Lundteigen with the results given below:

Analyses of Trenton Limestone.

	I	II	III	IV	V	VI
Silica, SiO_2	7.28	2.25	46.34	8.98	5.00	54.90
Alumina and Iron oxides $\left\{ \begin{array}{l} \text{Al}_2\text{O}_3 \\ \text{Fe}_2\text{O}_3 \end{array} \right\}$	1.27	1.32	19.90	2.58	2.07	25.50
Lime, CaO	46.93	49.66	10.27	41.32	50.22	.41
Magnesia, MgO	2.58	3.24	2.13	5.80	.85	.30
Alkalies by difference.....76	9.55
Sulphur, S.....	.3901	.00	.85	.24
Loss on ignition $\left\{ \begin{array}{l} \text{H}_2\text{O} \\ \text{CO}_2 \end{array} \right\}$	40.10	42.80	13.90	40.00	40.25	9.10
	99.25	99.27	92.55	98.68	100.00	100.00

- I. Beds 8 and 9, Specht Ferry Section.
 II. Bed No. 6, Specht Ferry Section.
 III. Bed No. 5, Specht Ferry Section.
 IV. Bed No. 4, Specht Ferry Section.
 V. General sample of limestone, Specht Ferry Section.
 VI. General sample of clay, Specht Ferry Section.

While the amount of magnesia in certain of these beds is higher than is desirable, there is still a large amount of rock available which is not higher in that element than that elsewhere used. It is probable that careful search would locate even better beds at the same horizon farther north.

DEVONIAN LIMESTONES.

There are in Iowa beds representative of both Upper and Middle Devonian. The former includes the State Quarry beds in Johnson county*, and the Sweetland shales in Muscatine†. The larger portion of the Iowa section belongs to the Middle Devonian, which may be divided into three formations, the Lime Creek, Cedar Valley and Wapsipinicon. In various counties these formations have been subdivided and individual members have been mapped. The Lime Creek and Wapsipinicon formations each include some shale and magnesian rock, but in general the Devonian limestones in Iowa are characteristically free from magnesia.

Wapsipinicon formation.—This formation was first discriminated by W. H. Norton who has discussed it in considerable

* Calvin, S., *Geology of Johnson County, Iowa Geol. Surv., Vol. VII, pp. 33-104.*

† Udden, J. A., *Geology of Muscatine County, Iowa Geol. Surv. Vol. IX, pp. 247-388.*

detail and has mapped various subdivisions belonging to it in Linn*, Cedar† and Scott‡ counties. J. A. Udden has discriminated it in Muscatine county§, and Calvin has mapped certain members belonging to it in Johnson|| and Buchanan.¶ Details of the development of the formation may be learned from the reports cited. In the northern portion of the state there is an overlap, so that the Wapsipinicon is not represented. In general it may be stated that while the formation includes some shale and some very pure limestones, the magnesia is apt to be found abundant in almost any section and careful sampling will be necessary to determine the availability of the rock at any given point. The Fayette breccia, which forms one member of the Wapsipinicon, includes, near Rock Island, a very pure limestone, as is shown by the following analysis.

*Analysis of Fayette breccia.***

Insol.....	.42
Iron (as carbonate).....	.36
Lime (CaCO ₃)....	98.77
Loss, alkalies, etc.....	.45

On the other hand samples of the Otis and Kenwood beds from a railway cut two miles north of Cedar Rapids, showed so much magnesia as to preclude the use of the rock.

Cedar Valley Limestone.—The most important member of the Devonian of Iowa as measured either by areal extent or thickness is the Cedar Valley Limestone. It extends from Muscatine county on the Mississippi to the Minnesota line in a broad belt trending northwest. It has an estimated maximum thickness of 300 feet and rests to the southeast on the Wapsipinicon formation. To the northeast it comes by overlap to rest on the Maquoketa shale††. To the southwest it is in turn covered by rocks of the Mississippian series, while on the northwest the

*Geology of Linn County, Iowa Geol. Surv., Vol. IV, pp. 121-195.

†Geology of Cedar County, Ibid. Vol. XI, pp. 279-396.

‡Geology of Scott County, Ibid. Vol. IX, pp. 339-520.

§Geology of Muscatine County, Ibid. Vol. IX, pp. 248-333.

||Geology of Johnson County, Ibid. Vol. VII, pp. 33-116.

¶Geology of Buchanan County, Ibid. Vol. VIII, pp. 201-255.

**Geol. of Iowa (Hall) p. 372.

††Calvin, S., Geology of Howard County, Iowa Geol. Surv., Vol. XIII, pp. 49-62.

Lime Creek shales intervene between the latter and the Cedar Valley.

In the southern portion of the area of outcrop the Cedar Valley Limestone is characteristically a non-magnesian limestone, usually fine-grained in texture and breaks with a sharp conchoidal fracture. This phase of the formation is excellently exposed in Johnson county, and the following analysis was made by George Steiger, in the laboratory of the U. S. Geological Survey, from an average sample representing the rock quarried at Iowa City. These quarries exposed a total thickness of about fifty feet.

Analysis Devonian Limestone at Iowa City.

SiO ₂	3.08
Al ₂ O ₃	1.24*
Fe ₂ O ₃73
CaO.....	50.30
MgO.....	2.22
SO ₃06

Toward the north the limestone becomes more magnesian until in Howard county it is a massive dolomite which has been mistaken for the Niagara. About midway the rock has been extensively quarried at Independence and Waterloo where it is a soft, easily crushed limestone, apparently non-magnesian in character. At Waverly the rock is soft, thin-bedded and exposed to a total thickness of about fifty feet. Analysis of two separate beds, by Lundteigen, gave the following results:

Analyses of Devonian Limestone at Waverly.

	I	II
SiO ₂	46.34	2.25
Al ₂ O ₃ }	19.90	1.32
Fe ₂ O ₃ }		
CaO.....	10.27	49.66
MgO.....	2.00	3.24
SO ₃01	.00
Loss on ignition.....	13.90	42.80
Total	92.42	99.27

* With the Al₂O₃ is included any TiO₂ or P₂O₅ present.

Still farther north, in Mitchell county, the limestone has attracted attention because of certain beds being lithographic.* The following analysis, made by Mr. A. B. Hoen, suggests that some, at least, of the stone is sufficiently free from magnesia to be suitable for cement material.

Analysis Devonian Limestone, Mitchell County.

SiO ₂78
Al ₂ O ₃12
CaO.....	54.91
MgO.....	.07
Na ₂ O.....	.18
K ₂ O.....	.11
CO ₂	43.16
H ₂ O.....	.35

There are a number of fine exposures showing a thickness of ten to fifteen feet of the non-magnesian stone. Not all of it is free from cracks and crystals as is the lithographic layer, but it is similar in composition to the sample analyzed at the Gable and other quarries, there is practically no stripping, while in the vicinity is an abundance of loess clay.

Lime Creek Shales.—The uppermost member of the Devonian section of Iowa is well displayed in Cerro Gordo county, and has been discussed and mapped in Calvin's report on that area.†

He gives the following general section of the formations.

General Section of the Lime Creek Shales.

	FEET.
6. Calcareous beds, light gray in color.....	20
5. Magnesian shales and argillaceous dolomites ...	30
4. Limestone with slender <i>Idiostroma</i>	4
3. Fossiliferous, calcareous shales.....	20
2. Yellow, non-fossiliferous shales.....	10
1. Blue, non-fossiliferous shales	40

Nos. 1, 2 and 3 of this section make up the Hackberry member of the formation, while the remaining beds represent the Owen beds. The shales constituting the lower portion of this section are now in use at Mason City for the manufacture of

*Iowa Geol. Surv., Vol. XIII, pp. 292-352.

†Geology of Cerro Gordo County, Iowa Geol. Surv., Vol. VII, pp. 117-192.

clay goods, and are represented in the following analysis made by G. E. Patrick:

Analysis of Lime Creek Clay at Mason City.

	FEET.
Silica SiO_2	54.64
Alumina Al_2O_3	14.62
Iron oxide (calculated as Fe_2O_3)	5.69
Manganese oxide (calculated as MnO)76
Lime CaO	5.16
Magnesia MgO	2.90
Soda Na_2O	1.12
Potash K_2O	4.77
Carbonic acid CO_2	4.80
Hygroscopic water (expelled at 100°C.)85
Combined water (expelled by ignition)	3.74
Total	99.05

This analysis represents only the non-calcareous portion. The beds above contain considerable lime as noted in the section given. In the vicinity of Mason City where these beds outcrop there are extensive exposures of the non-magnesian beds of the underlying Cedar Valley, and it should be possible to combine the two to advantage.

CARBONIFEROUS LIMESTONES.

Carboniferous rocks underlie a large portion of Iowa. They include limestones, sandstones, shales and coals. The limestones are very rarely magnesian and because of this fact, as well as their excellent situation with reference to fuel and transportation facilities, it seems not improbable that time will see the development of a considerable cement industry based upon them. Of the three series into which the Carboniferous has been divided, two, the Mississippian and the Pennsylvanian are represented in this state. The Mississippian may be divided into the Kinderhook, Augusta and Saint Louis, each containing important limestone beds. The Pennsylvanian includes the Des Moines formation (lower Coal Measures) and the Missourian (upper Coal Measures). The lower Coal Measures includes most of the coal beds worked in the state, but very little limestone. The formation outcrops in a broad belt

between the limestones of the Mississippian series to the east and the calcareous shales and thin limestones of the Missourian formation. The general distribution of the Mississippian, Des Moines and Missourian beds is shown on the geological map of Iowa. The details as to character, thickness, etc., in any area may be learned from the appropriate county reports*.

Kinderhook limestone.—The Kinderhook forms the lowermost division of the Carboniferous of this state. It consists for the most part of a soft argillaceous shale which is exposed to a thickness of sixty feet at Burlington.† Above the shale are about fifty feet of sandstone and limestone belonging also to the Kinderhook. In general the beds are not well exposed, and in the southern area of outcrop are not likely to be of importance in cement manufacture, except as a source of clay to be mixed with the overlying Burlington limestones. Farther north, in Marshall county, there is an extensive development of limestone. The rock is quarried at Le Grande, and the following analyses by G. E. Patrick indicate that a considerable portion of the stone is suitable for cement manufacture:

*Reports upon counties in which the Carboniferous rocks are important will be found in the volumes of the Iowa Geological Survey as follows:

Appanoose, V, 361-438;	Mahaska, IV, 313-380;
Boone, V, 175-240;	Marion, XI, 127-198;
Dallas, VIII, 51-118;	Marshall, VII, 197-262;
Decatur, VIII, 255-338;	Mills and Fremont, XIII, 122-183;
Des Moines, III, 409-492;	Monroe, XIII, 353-433;
Fremont and Mills, XIII, 122-183;	Montgomery, IV, 381-462;
Guthrie, VII, 413-488;	Page, XI, 397-460;
Hardin, X, 241-314;	Polk, VII, 263-412;
Henry, XII, 237-302;	Pottawattamie, XI, 199-278;
Humboldt, IX, 109-154;	Story, IX, 155-246;
Jefferson, XII, 355-438;	Van Buren, IV, 197-254;
Keokuk, IV, 255-312;	Wapello, XII, 439-499;
Lee, III, 305-408;	Warren, V, 301-360;
Louisa, XI, 55-126;	Washington, V, 113-174;
Madison, VII, 489-540;	Webster, XII, 62-191.

†Weller, Stuart, Iowa Geol. Surv., Vol. X, p. 65.

Chemical Analyses of Le Grande Stone.

	I	II	III	IV
Silica and insol.....	.77	.96	1.24	1.22
Alumina Al_2O_305	.07	.18	.14
Iron Fe_2O_315	.26
Iron FeO09	.27	.09	.09
Manganese oxide (as MnO).....		.08		trace
Lime CaO	55.05	54.85	50.56	50.42
Magnesia MgO28	.28	3.70	3.96
Carbonic acid CO_2	43.62	43.30	43.79	43.85
Hygroscopic water (loss at 100°C.).....	.03	.09	.06	.04
Combined water (expelled by ignition).....	.13	.21	.15	.12
Phosphoric acid.....			trace	
Total	100.02	100.11	99.92	100.10

Probable Combinations.

	I	II	III	IV
Silica and silicates, iron, alumina, oxides, etc..	.95	1.37	1.74	1.72
Calcium carbonate.....	98.30	97.95	90.28	90.04
Magnesium carbonate59	.38	7.77	8.08
Water.....	.16	.30	.21	.16
Total	100.00	100.00	100.00	100.00

- I. Fine-grained oolite.
- II. Blue limestone.
- III. Iowa Caen stones.
- IV. Stratified limestone.

Associated with these beds are certain others which are more magnesian, but which happen to be in demand as building stone. Possibly a combination of industries could be based on this association. In Hardin county there is a considerable thickness of the rocks with some associated shale. Still farther to the north and west the Kinderhook outcrops, but without exposing any great thickness. While much of the Kinderhook limestone is magnesian, it is believed that in localities where other conditions are favorable, the formation warrants prospecting and testing.

Augusta formation.—The Augusta includes beds which have been widely known as the Keokuk and Burlington limestones together with a portion of the Warsaw. The formation consists for the most part of coarse, crinoidal limestone, white, non-magnesian, and with chert in nodules along bedding planes.

The limestone is associated with abundant argillaceous shale, and often outcrops in steep bluffs, at the foot of which the shales of the Kinderhook are available. The beds are best exposed in Lee and Des Moines counties, but occupy portions of Louisa, Washington, Henry and other counties in the southeast part of the state.

At Burlington, in the south bank of the Cascade Hollow the following section was measured by Mr. T. E. Savage:

Cascade Hollow Section.

	FEET.
7. Fine-grained, homogeneous soil material without pebbles, dark-colored above grading down to yellow below.....	4
6. Clay with pebbles and small bowlders of granite and greenstone, reddish-brown.....	6
5. Limestone, much decayed, in layers one to four inches thick, numerous chert nodules.....	5
4. Chert.....	$\frac{3}{4}$
3. Limestone, crinoidal, coarse-grained, layers four to eight inches thick	4
2. Limestone, crinoidal, with chert nodules.....	1
1. Limestone, coarse, crinoidal; at places massive, at others weathering into layers three inches to one foot in thickness, containing numerous fossils	10

An average sample of this limestone was analyzed by George Steiger in the laboratory of the U. S. Geological Survey with the following results.

Analysis Burlington Limestone.

SiO ₂	5.18
*Al ₂ O ₃ }87
Fe ₂ O ₃ }	
CaO.....	52.16
MgO.....	.40
SO ₃00

The beds outcropping at this point are thoroughly representative of the Burlington limestone, the **most important** division of this formation. Greater thicknesses are exposed at other points and the total thickness has been estimated to be about two hundred and fifty feet.

*This figure includes any TiO₂ or P₂O₅ present.

St. Louis Limestone.—The St. Louis is one of the most widely distributed formations in Iowa. It rests on the Augusta and lies unconformably below the Des Moines formation. On account of its relation to the coal beds it has been carefully mapped and extensively studied. It includes three minor divisions, the Pella beds, the Verdi beds and the Springvale beds. Of these the first named is much the most important from the present point of view. The Verdi and Springvale beds have limited areas of outcrop and are usually not suitable in composition for cement manufacture. The Pella beds on the other hand outcrop widely and are, in composition, excellently adapted to this purpose. They fringe the productive coal measures on the east and occur as scattered inliers within the general area of outcrop of the coal beds. This results from the pronounced unconformity between the Des Moines and the St. Louis, hills of the limestone rising like islands above the lowest coal beds.

The Pella beds usually show an upper portion consisting of calcareous marl with some thin beds of limestone. This facies is ordinarily eight to ten feet thick. Below it are beds of fine-grained, blue to gray limestone breaking with clean conchoidal fracture and usually thin-bedded. The rock is very rarely magnesian and the analysis quoted below is quite representative. The sample was taken from the Chilton quarry at Ottumwa, by Mr. T. E. Savage. The beds exposed at this quarry are noted in the following section:

Chilton Quarry Section.

	FEET.
13. Fine-grained, dark colored, pebbleless soil....	1
12. Clay, reddish-brown, with pebbles	3
11. Sandstone, brown, iron-stained, mostly incoherent, but in places indurated (Des Moines)	10
10. Calcareous shale, weathering into small bits, very fossiliferous.....	3
9. Limestone, dense, fine-grained, gray.....	2½
8. Limestone, shaly, soft, weathering readily, similar to No. 10.....	2
7. Limestone, dense, fine-grained, gray.....	1½
6. Shale, calcareous.....	3
5. Limestone, hard, fine-grained, gray, fossiliferous	1

	FEET.
4. Limestone, dense, bluish.....	1
3. Limestone, dense, fine-grained, bluish-gray, in part massive, in part thin-bedded, fossiliferous	4
2. Limestone, hard, gray.....	1½
1. Limestone, dense, gray.....	1½

An average sample of the limestone and marl here was analyzed in the laboratory of the U. S. Geological Survey, by George Steiger, with the following results.

Analysis of St. Louis Limestone at Ottumwa.

SiO ₂	6.83
Al ₂ O ₃	2.12*
Fe ₂ O ₃54
CaO.	49.54
MgO.....	.07
SO ₃13

Samples of limestone from Pella, Tracey, Oskaloosa and Humboldt have also been analyzed with the following results:

	I	II	III	IV
SiO ₂	4.92			
Insol.....		1.57	4.01	.91
Al ₂ O ₃	} 3.39 }	.49	.13	.48
Fe ₂ O ₃17	.46	.73
CaO.....	47.50			
CaCO ₃		94.60	95.30	97.98
MgO.....	.00	3.17	.00	
Alkalies.....				
SO ₃	2.09			
CO ₂	} 38.10 }			
H ₂ O.....				

- I. Limestone, Pella, Lundteigen, Anal.
- II. Limestone, Tracey, Murray, Anal.
- III. Limestone, Oskaloosa, Murray, Anal.
- IV. Limestone, Humboldt, Murray, Anal.

*This figure includes any TiO₂ or P₂O₅ present.

Analyses of limestone and interbedded shale from the mouth of Lizard creek in Webster county, were made by Mr. Lundteigen, with the following results:

	CaCO ₃	CaSO ₄
3. Upper; limestone, 2 feet	88.75	.28
2. Middle, shale, 2 feet	53.25	2.46
1. Bottom, limestone, 2½ feet	88.75	.17

A cement made from this material gave the following analysis and on test showed satisfactory color, strength and setting properties:

Analysis Fort Dodge Cement.

Silica	25.52
Alumina and iron	8.80
Lime	63.40
Magnesia	1.19

The material from the Pella exposures has been made up into a cement which has good color, is sound on glass, sets very quickly and has satisfactory strength. The results of these tests, together with the fact that limestone of the same age and character is being extensively used at St. Louis, Missouri, makes it certain that this formation can be relied upon to furnish the calcareous element wherever other conditions are favorable to the establishment of cement plants.

Des Moines formation.—The Des Moines (lower Coal Measures) contains very little limestone. Its principal importance in the present connection arises from the coal and clay which make up so large a portion of the formation. The clays and shales are extensively used in the brick making industry. They are available over wide areas and may prove of service in connection with limestones of the formations above and below. The following analyses are typical of these clays:

Analyses of Coal Measures Shales and Clays.

	I	II	III
SiO ₂	53.08	64.41	53.86
Al ₂ O ₃	17.71	20.43	26.28
Fe ₂ O ₃	8.64	5.88	4.32
CaO	4.05	.34	.12
MgO94	1.71	.43
Na ₂ O	3.70	} 1.90 {	.43
K ₂ O	1.25		2.52
SO ₃			1.22
CO ₂	2.53		
H ₂ O { (combined)	6.77	3.93	3.02
{ (free)		1.27	
Undter. and ignition	1.33		8.06

I. Brick clay, Fort Dodge.

II. Brick clay, Des Moines, C. O. Bates, Analyst.

III. Brick clay, Ottumwa, J. B. Weems, Analyst.

Near the middle of the Des Moines formation there are a series of strata which have been called the Appanoose beds. These have been mapped and discussed in connection with the report on Appanoose county, and the outcrop of the "Fifty-foot" limestone, one of their important members, is shown on the accompanying map. The Appanoose beds include the Mystic or Centerville coal and certain associated shales and limestones. The latter are known locally, from their relations to the coal, as the "Bottom rock," "Cap rock," "Thirteen-foot limestone," and "Fifty-foot limestone." The beds are thin, usually from four to six feet in thickness, but near Rathbun and Clarkdale the Fifty-foot rock reaches a thickness of ten to fifteen feet. It is a soft limestone, easily crushed, and because of its close association with clay and a very good coal bed, is probably of value. Analyses show that it is practically free from magnesia and runs from 74 to 93 per cent in calcium carbonate. The following analysis by Lundteigen is representative:

Analysis Fifty-foot rock, Rathbun.

SiO ₂	9.90
Al ₂ O ₃ {	6.40
Fe ₂ O ₃ {	
MgO.....	trace
CaCO ₃	83.37

Missourian formation.—The southwestern portion of Iowa is underlain by the rocks of the Missourian formation or upper Coal Measures. In contrast with the lower Coal Measures or Des Moines formation, the Missourian includes considerably less sandstone and very little coal. The beds are mainly shales and limestones. The latter are almost entirely free from magnesia, are occasionally somewhat earthy and are usually free from chert, and easily ground. They are accordingly well adapted to cement manufacture and indeed the equivalent beds are now in use at Iola, Kansas. The individual members of the Missourian formation have not been mapped in Iowa, though they are discussed in the county reports. The most important limestone lies at the base of the formation and its outcrop is accordingly indicated on the geological map by the eastern edge of the formation. This limestone, which is variously known as the Winterset, Earlham and Bethany, is discussed in some detail in the Madison county report.

The Bethany limestone in Madison county includes four separate ledges occurring in the following order and thickness: Fusulina, twenty-five feet; Winterset, twenty feet; Earlham, twenty-one feet; Fragmental, ten feet. These ledges are separated by shale beds, usually ten to twenty feet in thickness, and in part calcareous. The rocks are quarried at various points, particularly Earlham, Winterset and Peru, and the same ledges have been recognized as far south as Decatur county on the Missouri boundary.

Analyses of individual ledges at Peru, made by Lundteigen, show a lime content ranging from 60.50 per cent to 83 per cent. A cement mixture made from them gave 75.50 per cent CaCO_3 . At Earlham the following section was measured by Mr. T. E. Savage, and an analysis of an mixed average sample of the stone was made in the laboratory of the U. S. Geological Survey by George Steiger. The results are given below:

CEMENT MATERIALS OF IOWA.

Section of Robertson Quarry, Earlham.

	FEET.	IN.
19. Dark colored, fine-grained, pebbleless soil.	1	
18. Reddish boulder clay with pebbles and quartzite fragments.....	1	6
17. Yellowish colored, soft, shaly limestone which disintegrates readily.....	4	
16. Layer of very hard, light gray, fine-grained limestone.....		7
15. Narrow layer of softer limestone with less perfectly comminuted fossil fragments..		2
14. Ledge of hard, white limestone, fine-grained, separating in places into three or four uneven layers.....	3	
13. Soft, calcareous shale which weathers rapidly into fine bits.....		4
12. Dense, gray limestone, fine-grained, fossil fragments abundant but indistinct.....		6
11. Gray shale like No. 9.....		1½
10. Layer of hard, gray limestone.....		2
9. Band of soft shale.....		1½
8. Dense, fine-grained, light gray limestone, in places massive, again separating into two layers of about equal thickness....	1	8
7. Shale, soft, gray in color, and quite calcareous.....		6
6. Layer of impure limestone, grayish-yellow in color.....		2½
5. Band of soft, gray, calcareous shale.....		7
4. Ledge of hard, fine-grained, light colored limestone, imperfectly separated into three uneven layers.....	1	3
3. Massive layer, separating in places into two uneven layers with shaly partings between them, and such partings of shale separating No. 3 from No. 4 above and from No. 2 below	1	4
2. Ledge of gray limestone	1	3
1. Layer of gray limestone.....	1	8

Analysis Earlham Limestone.

SiO ₂	10.92
Al ₂ O ₃	1.77*
Fe ₂ O ₃60
CaO.....	47.66
MgO.....	.75
SO ₃	None.

* This includes any P₂O₅ or TiO₂ present.

The beds above the Bethany have not been as carefully studied though they are apparently similar in composition and character. The next higher limestone, the DeKalb, yielded the following on partial analysis by J. B. Weems:

Analysis DeKalb Limestone.

CaCO ₃	91.96
MgCO ₃	1.99
H ₂ O.....	.07

SUMMARY.

It is believed that the data presented bear out the assertion that there are many points in Iowa at which materials suitable for cement manufacture are available. The marls are not now known to be important and may never prove to be. Chalk suitable in all particulars may be found along the Sioux river north of Sioux City. As this is a soft, easy grinding material, it is a favorite among cement manufacturers. The question of the advisability of establishing a plant in this district must be determined by consideration of manufacturing costs, of market and transportation facilities.

In regard to the limestones the following general considerations are important. Iowa is largely a drift covered state and within the broad areas shown upon the map as underlain by the various limestones there are really only a limited number of outcrops. Even where outcrops occur, the overburden is in many cases so thick as to entail prohibitive stripping costs. The best situations are in the valleys, usually where some important tributary joins the main stream. Fortunately, many of the railway lines follow valley routes.

The Trenton limestone, which occurs in the Driftless Area, is found usually in rather steep bluffs; a fact due to the resistant character of the dolomite usually found above it. As compared with the other limestones of the region the Trenton is more likely to carry magnesia in excess, but it is, on the other hand, practically free from chert, is often somewhat earthy in composition, and is intimately associated with shale. As already noted, the similar and approximately equivalent beds in the Lehigh district of Pennsylvania and New Jersey are a very important source of cement material.

The Devonian limestones are in large measure free from both chert and magnesia, though outcrops in the northern part of the state need careful examination to make sure of the absence of the latter. As contrasted with both the Trenton and the Carboniferous limestones they are in the main harder, and this will to some extent influence the cost of grinding.

Of the Carboniferous limestones the Kinderhook are in most situations too magnesian and the Augusta too full of chert for easy use, though it is probable that some suitable material can be found in each formation. The Pella beds of the St. Louis, and the Winterset and other limestones of the Missourian are entirely suitable as regards composition, freedom from chert and grinding qualities. Equivalent beds are now in use in Missouri and Kansas. These limestones are, furthermore, excellently situated as regards fuel and clay. The productive Coal Measures (Des Moines formation) outcrop in a broad belt between the two and often Pella beds and shales of the Des Moines occur in the same section. Where the shales are absent, loess, such as is elsewhere used, is nearly everywhere present.

RELATIONS TO FUEL AND MARKETS.

The area of the productive Coal Measures, Des Moines formation, is shown on the geological map of Iowa. It will be seen that the coal mines are so situated as to afford cheap fuel to most of the limestone localities. This is quite important since the fuel cost forms approximately 30 per cent of the total manufacturing cost. Iowa coal, while not of the highest grade, is still well adapted to cement manufacture. The following analyses indicate the approximate composition of a few of the coal beds. These analyses and tests were made at the Iowa State College of Agriculture, and are published in the report on Monroe county.*

*Iowa Geol. Surv., Vol. X.If, p. 414.

Analyses of Iowa Coals.

	Volatile Combusti- ble,	Fixed Com- bustible,	Total Com- bustible,	Ash.	Sulphur.	B. T. U.
Average five Monroe county coals...	42.32	46.81	89.13	10.13	4.10	11,922
Centerville Block Coal Co., Appa- noose county.....	37.79	54.85	92.64	7.36	3.29	12,681
Corey Coal Co., Webster county....	37.98	47.98	85.96	14.04	5.90	12,431
Des Moines C. & M. Co., Polk county.	45.62	50.29	95.91	4.09	2.74	12,041
Whitebreast Fuel Co., Pekay, Ma- haska county.....	46.06	46.89	92.95	7.05	2.81	13,050
Carbon Coal Co., Willard, Wapello county.....	36.94	54.20	91.14	8.86	2.85	12,245
Average 22 Illinois coals.....	35.11	51.91	87.02	12.77	3.02
Pocahontas coal, Virginia.....	18.23	75.08	93.31	6.69	.60

In the above tables the Pocahontas coal is quoted for comparison, and the Illinois coals are noted since, in event of the Trenton limestone being used, coal would probably be drawn from Illinois rather than Iowa. Many additional analyses will be found in the special report on the coal deposits forming volume II of the reports of the Iowa Geological Survey, and some additional data in the Twenty-second Annual Report of the U. S. Geological Survey.*

In the majority of the newer cement plants of the United States, powdered coal is used as a fuel. The Iowa coals are well adapted to this method of firing. The methods of burning cement and the cost of fuel have already been discussed.

The relations to transportation lines are perhaps clearly enough indicated by the map. It is sufficient to notice that there are several promising localities along the Mississippi river where the latter could be utilized directly and would in addition act as a regulator of railway rates. The main railway lines of Iowa run either east-west or southeast-northwest and much of the freight originating in the state, aside from agricultural products, moves to the north and west. Any cement plant which may be established would find a ready market in the same direction. Iowa, itself, affords a very considerable market for

* The Western Interior Coal Field, Twenty-second Ann. Rept., U. S. Geol. Surv., pt. iii, pp. 333-366.

cement, and an Iowa cement plant would have considerable advantage in reaching an important and growing market to the north and west.

Despite the large amount of material available, and the convenient fuel and transportation facilities, no Portland cement plants have been established in Iowa. In neighboring states a number are in operation and others are building or in contemplation.

CEMENT PLANTS IN NEIGHBORING STATES.

One of the oldest plants in the middle west is located at Yankton, S. D., where the Western Portland Cement Company makes use of the chalk and clay found in the Cretaceous. In Illinois there are three large and well equipped plants near LaSalle, using a Coal Measure limestone similar to the "Fifty-foot" rock, outcropping in Appanoose county, in connection with ordinary Coal Measure shale. There is also a Portland cement plant in Chicago, in connection with the works of the Illinois Steel Company. In Missouri there are three plants. At Saint Louis, loess, Coal Measure shale and Saint Louis limestone are used. At Louisiana the Louisiana limestone will be used in a new plant now being erected. At Hannibal the Atlas Portland Cement Company has a large plant running on the Burlington limestone and Kinderhook shales. In Kansas there are two plants at Iola, one of which is very large, which manufacture an excellent grade of cement from beds equivalent to those occurring in the Missourian formation as mapped in Iowa. These plants have heretofore had the advantage of a cheap fuel in the natural gas of that field. As the gas pressure is steadily decreasing they will, doubtless, eventually, be compelled to use coal for fuel.

In addition to these plants, there are natural cement plants at Mankato and Austin, Minnesota, at Milwaukee, Wisconsin, Utica, Illinois and Fort Scott, Kansas. To the north and west the possible trade territory is thus practically unoccupied. In North Dakota there is a small plant devoted to the manufacture of natural cement, and in Colorado and Utah there is one Portland cement plant each. In view of these favorable trade conditions it would seem that one or more Iowa plants might confidently be expected to prove successful.