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HENRY LANDES, State Geologist

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Cement Materials and Industry
IN THE
State of Washington

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LETTER OF TRANSMITTAL.

Governor Ernest Lister, Chairman, and Members of the Board of Geological Survey:

GENTLEMEN—I have the honor to submit herewith a report entitled "Cement Materials and Industry in the State of Washington," by Solon Shedd, with the recommendation that it be printed as Bulletin No. 4 of the Survey reports.

Very respectfully,

HENRY LANDES,

State Geologist.

University Station, Seattle, Oct. 1, 1912.

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PREFACE.

Work on the cement materials of Washington was begun in the summer of 1909, the whole of the field season of that year being devoted to the study of the limestone, shale and clay deposits. Practically all of the limestone deposits in the state, as well as the deposits of shale or clay found associated with this limestone, were examined and samples for analyzing collected.

In the spring of 1911 the Board of Geological Survey decided to determine and map in so far as possible the distribution and extent, especially of the limestone deposits of the state and the field season of 1911 was spent mostly in Stevens, Ferry and Okanogan counties on this work. The lack of anything like good maps for much of the area covered and of the time and money to make such maps has resulted in only an approximation of the extent of the deposits being shown.

The samples from which the chemical analyses given here were made are representative ones in so far as such could be obtained. These analyses, however, represent only in a very general way, in most cases at least, the composition of the deposits and should not be considered in any except this way. In many cases the deposits are large and it was not practicable to take enough samples to prove absolutely the character of the deposit as a whole. It is hoped, nevertheless, that the analyses given here may be a help in showing where in all probability good cement materials may be found.

I take pleasure in here acknowledging the many courtesies received from people with whom I have had dealings in connection with this work. In practically every case they have been very willing and glad to help in every way that they could.

Acknowledgments are due to Mr. Arthur G. Smith, Secretary and General Manager of the Washington Portland Cement Company, for photographs and description of the plant; to Mr. S. L. Barnes, Secretary of the Superior Portland Cement Company, for photographs and description of the plant; to Mr.

Dann R. Brown, Secretary and Assistant Treasurer, Inland Portland Cement Company, for photographs and description of the plant; to Mr. H. W. Wood, Chief Engineer, International Portland Cement Company, for photographs and description of plant; to Mr. James C. Muir, Superintendent, Olympic Portland Cement Company, for photographs and description of the plant; to Mr. H. R. Blauvelt, Sales Manager, Idaho Portland Cement Works, Limited; to Mr. F. W. Graham, West Industrial and Immigration Agent, Great Northern Railway Company, for information furnished in regard to limestones.

Much information of a general character bearing on the manufacture of Portland cement and the kind of materials that may be used in its manufacture has been included in this report, in the hope that it may be of value in helping to develop the cement industry in Washington. Reports of State Geological Surveys and technical treatises of various kinds have been freely consulted and data taken from them. Credit for such information is given in each case in the foot note references, but I desire also to make a general acknowledgment here.

Nearly all of the chemical analyses given in this report were made by Mr. A. A. Hammer, who was also associated with me in all of the field work. Mr. Roy W. Merrit was also an assistant in the field work during the summer of 1911.

S. SHEDD.

State College of Washington,
Pullman, July, 1913.

CHAPTER I.

GENERAL CONSIDERATION OF THE HYDRAULIC CEMENTS.

The term hydraulic cement has reference to those mortars which harden in water—as well as in the air—and would distinguish these from those which harden only in the air—such as ordinary lime mortar and plaster. This hydraulic property is due to the formation, during manufacture, of compounds of lime with silica, alumina and iron oxide. These compounds, however, vary more or less in the different kinds of cements and limes and, therefore, the hydraulic properties vary.

When pure limestone (CaCO_3) is heated its carbon dioxide (CO_2) is driven off, leaving pure calcium oxide (CaO) which is quick or common lime. Many limestones contain more or less impurities, as silica, alumina, or iron oxide, and when these are heated, the results are very different and various compounds of lime with silica, alumina and iron will be formed. When this happens the burned mass will not slake when water is poured on it, but when this burned mass is finely ground and mixed with water it has the property of hardening and is a hydraulic cement.

Based on the above definition of cement, we may classify hydraulic materials into the following:

1. Pozzuolana cements.
2. Hydraulic limes.
3. Natural cement.
4. Portland cement.

All of these harden by a process of hydration and require water for the initial set.

1. Pozzuolana cements are the oldest known hydraulic mortars, having been used extensively by the Romans for their gigantic aqueducts and hydraulic work of various kinds. The pozzuolana of the ancients was made by mixing cinder-like vol-

d. c. & quick lime

canic fragments, found in large quantity at Pozzuoli near Naples, Italy, with slaked lime. The pozzuolanas alone do not possess hydraulic properties to any great extent, the lime being absolutely necessary to produce this property. The pozzuolana contains soluble or hydrous silicic acid, which readily unites with the lime hydrate when the two are mixed. Any material which will furnish silicic acid in a condition such that it will be readily available for combination with lime hydrate may be used for this purpose.

Slag cement, an artificial pozzuolana, has found quite an extensive application of late years. This is made from granulated blast furnace slag mixed and ground together with lime hydrate. Blast furnace slag cooled slowly would represent an artificial basic igneous rock and would have scarcely any hydraulic properties. When cooled quickly, however, by water, it has a considerable amount of soluble silicic acid and when intimately mixed with lime hydrate forms a strong hydraulic cement.

2. The hydraulic limestones are those which contain more or less clay and sand intimately mixed by nature with lime carbonate. These limestones generally have from 18 to 25 per cent. of clay and sand with at least 70 per cent. of calcium carbonate and magnesium carbonate. When burned and mixed with water they slake and generally harden to a compact mass, the greatest hardness being obtained when the mortar is in water. On account of the fact that the burned hydraulic limestone slakes when water is added it is not necessary to grind it.

3. Natural cements, like hydraulic limes, are also made from naturally blended mixtures of calcium and magnesium carbonates and clay with usually some free silica. The amount of lime and magnesium in these is less than in the hydraulic limes and ranges from about 50 to 70 per cent. When burned these rocks form a more or less porous and friable mass which will not slake in water when in the lumpy condition and hence must be ground to a powder. This, however, may be easily done by means of cheap machinery. The percentage of clay in the

natural or Roman cement is greater than in the hydraulic limes, being from 30 to 50 per cent. The strength of these cements is greater than that of hydraulic lime but not so great as that of Portland cement.

4. Portland cement is by far the most important and widely used of any of the hydraulic cements. This, unlike the natural or Roman cement and the hydraulic limes, is made from an artificial mixture of limestone (CaCO_3) and clay in certain proportions. This is burned at a high enough temperature so that vitrification ensues and then finely ground, when it shows very marked hydraulic properties, having a high tensile and crushing strength and a high cementing power. On account of the fact that the raw material has to be finely ground before burning, that it has to be burned at a high temperature, and then the burned material again finely ground, it is natural that Portland cement should be a more expensive material from which to make mortar. Portland cement, however, is coming into very general use largely on account of its greater strength and durability and the fact that for most purposes it makes a better mortar.

THE CONSTITUENTS OF THE HYDRAULIC COMPOUNDS.

The main constituents of all hydraulic cements of whatever kind are silicates of lime or magnesia. These, however, are always associated with alumina or ferric oxide. These may be assumed to combine with the lime and form aluminates and ferrates of calcium or to enter into the calcium silicate with the formation of a complex silicate.

The alumina and iron each acts in much the same way in modifying the properties of the simple calcium silicate. The alumina appears to regulate the rate of hydration reaction which without it is very slow, in fact too slow to be of practical application. When the amount of alumina is greater than 10 per cent. this cement is very quick setting and has a low tensile strength. The aluminates are hydraulic in themselves and when present in small amounts this property helps to increase the total strength of the silicates.

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The alumina and iron are also important in determining the melting point of the compounds. In order to secure slowness of set and greater ultimate strength, small amounts of alumina are desirable. As alumina, however, aids very materially in securing a low temperature at which the mass will clinker, it is not practical to reduce the amount below a certain minimum. Too much alumina will also give a very easily fusible, sticky mass and may cause trouble in the kiln. Iron also acts as a flux and lowers the temperature at which the mass will fuse. This is an important point in the burning of the highest grade of cement.

SILICA.

Silica is one of the very common substances occurring in nature and forms a large part of the crust of the earth. It occurs in nature either in the crystalline or the amorphous form or combined with various bases to form the silicate minerals. It may be used in any of these forms to a certain extent at least in the manufacture of cement.

Silica, next to lime and magnesia, is the most important constituent of any of the different kinds of cements and is in the next largest proportion. In some few cases the amount of silica in a natural cement is less than the amount of magnesia, but in all other kinds of cement the amount of magnesia is very small as compared with the amount of silica. Portland cements usually have from about 19 to 25 per cent. of silica, while 4 to 5 per cent. of magnesia is considered as the maximum.

Crystalline silica in its various modifications is known as quartz. This is a very important constituent of many of the igneous rocks and when the other constituents of these rocks, which are mainly silicate minerals, decompose and break down the rock, the quartz remains unchanged chemically and finally, after having been transported for greater or lesser distances by running water or by winds, is deposited as beds of sand.

Quartz crystals when pure are perfectly colorless, have a specific gravity of 2.653, and a hardness the same as that of well tempered steel. Quartz may be of almost any color on ac-

count of the various impurities occurring in it. It is practically insoluble in the acids with the exception of hydrofluoric, but is attacked more or less readily by alkaline solutions, especially if the solutions are heated. When fused with sodium or potassium carbonate, it forms compounds which are easily dissolved.

Heating quartz to red heat or above produces molecular changes and the quartz expands. Heat is also a very important factor in bringing about a union of the silica with the various bases. When anhydrous silicon dioxide is highly heated it becomes a very active and powerful acid and unites readily with the various bases to form the large group of minerals known as silicates. The physical condition of the silica, that is whether the particles are large or small, is a very important factor in governing the chemical reactions taking place. The finer the particles the more readily are the combinations brought about. Bleininger,* after a series of experiments on the range of size allowable for the quartz fragments in the preparation of hydraulic mixtures, makes the following statement: "Quartz grains whose diameter averages more than 0.005 of an inch are practically inert, since their reaction with the basic substance remains only superficial. This question of size is of the utmost importance in practice, since for all artificial cements the quartz must be ground to the required fineness, an operation which means a certain expenditure for power and wear and tear of machinery."

Silica in the amorphous form occurs in nature in the hydrous or the anhydrous condition; that is, with or without water as a constituent part of the compound. Some of the sources from which amorphous silica may be derived are chalcedony, opal, diatomaceous earth, santorin earth, trass, and pozzuolana. These are proving of most importance when used as sand in cement that is to be used where it will be subjected to sea water. The silica in these substances will unite with any free lime, especially the hydrated form, that may be present in the cement and produce silicates of lime.

The most important source of silica for use in the manu-

*Geological Survey of Ohio (4th Series) Bulletin 3, p. 29.

facture of cement is the silicate minerals. In these minerals the silica and the different bases are united and when they are used as the source of silica in the manufacture of cement they must be brought into such a condition that the silica may unite to form new compounds. When silicate minerals are heated to certain temperatures they are broken down and the ingredients are liberated and are then free to form new combinations and hence new mineral substances.

While the number of silicate minerals is very large, many of them are quite complex in composition and contain substances that are detrimental to the cements. Others, again, have the constituents needed in the cements but they are not in the proper proportions, so that really only a very few of these minerals can be used as a source of silica in the manufacture of cement. Kaolinite is a silicate of alumina with water. Silica and alumina are each of them essential constituents of a cement, but in a cement they must occur only in certain proportions and in kaolinite this proportion is different from what it should be in the cement, the amount of alumina being high and that of the silica relatively low. On account of this only small amounts of this mineral could be used without producing a cement too high in alumina.

In many cases it is necessary in order to obtain the proper proportions between the different substances in the cement mixture to use a mixture of different silicate minerals or by supplying the extra silica needed in the free or uncombined form.

The ultimate strength of the cement is usually considered as depending, at least in a large measure, on the amount of calcium trisilicate present. Therefore, any increase in the percentage of silica, up to a certain point in the mixture, should increase the final strength of the cement. This would also increase the setting time. The addition of silica will also raise the temperature at which the material will clinker and produce a good cement.

ALUMINA.

The amount of the alumina varies considerably in the various kinds of cements. In Portland cement it is between 5 and

10 per cent.; in natural cement it is from as low as 2.34 to as high as 19.79 per cent., and in slag cement it is about 10 to 14 per cent. When the percentage of alumina rises above a certain point the cement becomes very quick setting and at the same time the tensile strength decreases. The strength of the cement is due to the calcium silicate and any increase in the amount of alumina necessarily causes at least a relative decrease in the amount of calcium.

Experiments have been performed by uniting calcium oxide and alumina alone to show how alumina affects the hydration of cements. "Professor Zulkowski* thus found that a mixture of calcium oxide and alumina corresponding to the formula CaOAl_2O_3 , burnt for eight hours when mixed with water, set in two minutes and hardened to a very hard mass over night; in three months it became so hard that it could hardly be scratched with a knife. A mixture of the formula $2\text{CaOAl}_2\text{O}_3$ heated to vitrification also hardened with great rapidity in two to three minutes and assumed an extraordinary hardness after being in water three months."

"Zulkowski† prepared a cement from Zittlitz kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) corresponding to the formula $2(2\text{CaOSiO}_2) (2\text{CaOAl}_2\text{O}_3)$. On burning this mixture to vitrification a white porcelain-like body was produced which, when powdered and mixed with water, set in fifteen minutes. After ninety minutes the cement became extremely hard and after a few months it was found to be still harder. Zulkowski did not test this cement for constancy of volume. By the addition of quartz he prepared other white cements with the same lime silica ratio (2CaOSiO_2) which were all excellent cements."

Experiments along this same line have been carried on by a number of other investigators and much the same results obtained. The results all show very clearly that it is necessary to have alumina present in cements.

*Sonderabdruck aus "Die Chemische Industry," 1901 (Quoted) Geological Survey of Ohio (4th Series) Bulletin 3, pp. 32, 33.

†Bleininger, Geological Survey of Ohio (4th Series) Bulletin 3, p. 33.

FERRIC OXIDE.

There has been great differences of opinion in the past as regards the behavior of ferric oxide when combined with lime or lime and silica. Le Chatelier, from his experiments, concluded that when ferric oxide and calcium carbonate were burned together they yield a product which slakes with water and has no hydraulic properties. Schott, on the other hand, prepared cements containing only lime, silica, and ferric oxide, which showed excellent hardening qualities. From his experiments he concluded that alumina could be entirely replaced by ferric oxide without in the least decreasing the hydraulic properties of the cement. S. B. and W. B. Newberry, from their studies on this same subject, concluded that ferric oxide and alumina act in a similar manner in promoting the combination of silica and lime.

Zulkowski also made experiments in a most careful manner along this same line with the following results: "On burning the mixture CaOFe_2O_3 in the Seger furnace till partially fused it assumed a graphite appearance and when ground and mixed with water it formed a pat of a fine mahogany-like color. It set in four hours. After five hours more it was hard enough to be placed in water. After several months the pat became quite hard, but did not show as much strength as the corresponding alumina compounded. The mixture $(2\text{CaO})\text{Fe}_2\text{O}_3$ burnt to softening, which took place at white heat, showed a decided crystalline structure. After grinding and making up with water the pats set in five minutes and in one to two hours had become quite solid and hard. After one week in water they softened somewhat and lost their original strength. When dried in a desiccator they became harder again, but did not reach the hardness of the corresponding alumina compound. More favorable results were obtained with impure materials, that is, with reagents containing some silica and alumina."*

It appears that the compounds of iron and lime with silica are very similar to those of alumina, lime and silica, except that

*Bleininger, Geological Survey of Ohio (4th Series) Bulletin 3, p. 34.

they do not have such strong hydraulic properties. Lime silicate (3CaO) SiO_2 fuses only at extremely high temperatures. This, however, becomes very much more fusible if alumina is added and still more so when iron is added. When iron is entirely absent the temperature required to burn Portland cement is so high that it is not feasible to manufacture it in commercial quantities.

LIME.

Lime constitutes by far the largest ingredient of all hydraulic cements. It occurs in nature in large quantities mainly as calcium carbonate (CaCO_3). It varies in composition from almost pure calcite to the very impure forms. Pure calcite should contain 56 per cent. of calcium oxide (CaO) and 44 per cent. of carbon dioxide (CO_2). When calcium carbonated is heated to a temperature of about 750 degrees C. it begins to separate into calcium oxide and carbon dioxide, complete expulsion of the carbon dioxide taking place under ordinary conditions when a maximum temperature of 1040 degrees C. has been reached and in many cases a lower temperature is sufficient to bring about this result.

The amount of lime in cement varies considerably. In the Portland cements it ranges from about 58 to 65.5 per cent.; in the natural cements from about 30 to 50 per cent.; and in the slag cements from about 49.25 to 51.8 per cent. The more lime there is in a cement, upto a certain limit, the greater will be its strength. The limit theoretically for the lime will be reached when just enough is present to combine with all the silica and alumina. In actual practice, however, the maximum amount should not be present, as the mixing, grinding, and calcination are never absolutely perfect and on account of this the union of all the lime with all of the silica and alumina is not attained. On account of this fact, if the maximum amount of lime is present some free lime will remain after the mixture has been burned. On the other hand, if the mixture carries less than the theoretical amount of lime, the cement will carry some uncombined silica or alumina, so that it becomes a choice between free lime and free or

uncombined clayey material, and on account of the effect that each of these has on the cement, the latter is much the more desirable.

High lime cements are usually slow setting but reach their maximum strength in a short time. At the present time it is generally agreed that up to the limit of safety every increase in the percentage of lime in the cement mixture, other things being equal, will cause an increase in the strength of the cement. The amount of lime a Portland cement may contain depends to a very great extent upon the care with which the mixture of the raw materials is made. Poorly ground, imperfectly mixed raw materials would in all probability result in the production of cement carrying lime very much in excess of the maximum allowed, as shown by a chemical analysis of the raw materials of the mixture. The finer the particles of calcium carbonate the more closely in contact will they come with the particles of silica and alumina and hence the more readily will they unite with them. Over-limed Portland cements may be due then either to a wrong proportioning of the lime, silica, and alumina in the raw mixture or from poor manufacture, especially in mixing and burning.

MAGNESIA.

The carbonate of magnesia ($MgCO_3$) is the common form in which this substance occurs in the materials used in the manufacture of cements. Many limestones contain more or less magnesium carbonate. Magnesite or magnesium carbonate ($MgCO_3$), when pure is white, has a specific gravity of about 3, and is a little harder than calcite. It has 52.4 per cent. of carbon dioxide (CO_2) and 47.6 per cent. of magnesia (MgO).

The amount of magnesia (MgO) in the different kinds of cements in use at the present time varies much. In the natural cements it ranges from less than 1 per cent. to as high as 30 per cent. In American Portland cement it is from about 0.25 to 3.5 per cent. as shown by analyses.* Slag cements usually contain less than 3.5 per cent. of magnesia. Formerly it was thought

*Eckel, Cements, Limes and Plasters, pp. 577-579.

that if a Portland cement contained more than 2 per cent. of magnesia (MgO), it was too high in this substance, but now 4 to 5 per cent. is considered the allowable maximum. It has been shown, however, by Campbell and White that with very careful selection, proportioning and burning of the raw materials, good Portland cements can be made even when they contain as high as 10 per cent. of magnesia. R. Dyckerhoff, from a series of very careful experiments, the results of which were given to the German Association of Cement Manufacturers in 1895, concluded that magnesia when present in more than 4 per cent. caused a decrease in the strength of the cement and when more than 8 per cent. of magnesia was present cracking occurred. Le Chatelier considers magnesia to replace lime, but the Newberrys in their formula consider the magnesia to be inactive and not to replace lime.*

From the above it is very evident that there is still considerable difference of opinion as to what is the effect of high percentages of magnesia in Portland cement.

ALKALIES.

The amount of potash and soda in cement varies more or less, but is never very large. In Portland cement it ranges from practically nothing to about 2.5 per cent., usually, however, being less than 0.75 per cent. Experiments made by R. K. Meade†, indicate that at least one-half of the potash is lost in the kiln, while burning the cement, passing off in the kiln gases. Soda being much less volatile than potash would not suffer so great a loss in burning the cement.

“The addition of small quantities of either the carbonate or the hydroxides of potash and soda will cause cement to set quickly, and it is probable that the presence of any considerable quantity of alkali in cement would cause it to set quickly. When quick setting cement is due to the presence of the alkalies, the trouble can be remedied, to some extent, by raising the temperature of burning, thus volatilizing the alkali. Cements made from alkali waste often contain large quantities of potash and soda,

*Meade, R. K., *Portland Cement*, p. 29.

†*Portland Cement*, p. 30.

in some cases the amount reaching as high as 2.5 per cent. Butler states that instances have occurred in which these cements gave anything but satisfactory results, and the only fault that could be found with their chemical composition was a slight excess of alkali. In most cements the alkalies are present in such small quantities that their effects are of little hydraulic importance."*

SULPHUR.

The sulphur present in cement may be in any of a number of different combinations, the most important of which is gypsum or calcium sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). This is often added to Portland cement in small quantities in order to retard the set. The standard specifications allow manufacturers to use not to exceed three per cent. of gypsum. That is, the finished product should not show when analyzed more than 1.75 per cent. sulphur-trioxide (SO_3).

Meade† gives the following with regard to the effect of gypsum in Portland cement:

"The retrogression often met with in neat Portland cement briquettes is often attributed to the presence of calcium sulphate in the cement. My own experiments, however, made with cements to which no gypsum had been added and the same cement with the addition of 12 per cent. gypsum, do not indicate this, as, in most cases, where retrogression occurred in the cement to which sulphate had been added, it also occurred with the un-sulphated cement. Sulphates increase the strength of cement, and if they are present in larger amounts than 2 or 3 per cent., will unquestionably cause higher short time tests than the long period ones, though this may be due merely to the test pieces becoming brittle. The presence of sulphates in cement promotes soundness, or at least enables some cements to pass the accelerated tests."

CARBON DIOXIDE AND WATER.

The amount of these substances in freshly made cement is extremely small, as during the process of burning both the carbon dioxide (CO_2) and the water are nearly or entirely driven off, the amount remaining usually being less than 1 per cent.

*Meade, R. K., *Portland Cement*, p. 30.

†*Portland Cement*, p. 31.

Cement which has been stored for some time and allowed to season may contain as much as 3 or 4 per cent. of carbon dioxide (CO_2) and water (H_2O). This has been absorbed from the air and has a beneficial effect on the cement as is shown by tests on samples of freshly burned cement as compared with those made on the same material after it has "aged."

Standard specifications place no limit on the percentage of combined water and carbon dioxide. This is due to the fact that the loss on ignition gives no positive proof as regards the quality of the Portland cement. Under-burned cements may or may not show a high loss on ignition. This is due to the fact that it is possible to drive off all of the carbon dioxide and the water from the raw material and still not bring the mass to a temperature high enough to produce incipient vitrification necessary to form a sound clinker. Samples of under-burned clinker may show, on ignition, as great a loss of water and carbon dioxide as those of well burned cement.

OTHER COMPOUNDS IN CEMENT.

In addition to the substances already mentioned, cement may contain small amounts of Phosphorus pentoxide (P_2O_5), Titanic acid (Ti_2O_3), Strontium oxide (SrO), Ferrous oxide (FeO), and Manganous oxide (MnO). These substances all occur, however, in such small amounts in commercial cement that they have practically no effect on the setting properties of the cement.

The following amounts of these rarer constituents were found by Meade* in three Portland cements from the Lehigh district:

RARER CONSTITUENTS OF PORTLAND CEMENT FROM LEHIGH DISTRICT.

	CEMENT NUMBER		
	1	2	3
Titanic acid (Ti_2O_3).....	0.28	0.27	0.32
Ferrous oxide (FeO).....	0.23	0.16	1.11
Manganous oxide (MnO).....	0.06	0.08	0.09
Strontium oxide (SrO).....	0.08
Calcium sulphide (CaS).....	0.18	0.09	0.07
Potash (K_2O).....	0.50	0.48	0.59
Soda (Na_2O).....	0.26	0.31	0.38
Phosphorous pentoxide (P_2O_5).....	0.25	0.31	0.29

*Portland Cement, p. 42.

CHAPTER II.

RAW MATERIALS OF THE CEMENT INDUSTRY.

In this chapter the various raw materials that may be used in the manufacture of the different classes of hydraulic cements given in the preceding chapter, will be discussed. Of these different classes Portland cement is the most extensively used and is rapidly taking the place of natural cement.

RAW MATERIALS FOR POZZUOLANA CEMENT.

The pozzuolanic materials are of two general classes, the natural and the artificial.

NATURAL POZZUOLANA.

This class of cement is the oldest type of hydraulic cement and was originally made from material having as the main constituent a substance containing hydrous silicic acid. To this material slaked lime was added and a hydraulic cement was formed.

The natural pozzuolanic materials include all those natural substances which are capable of forming hydraulic cements on being mixed with lime without the use of heat. There are many materials that possess this property to a greater or less degree but only a very few of them have it in sufficient amount to make them valuable commercially.

The pozzuolanic materials are made up largely of silica and alumina, with more or less lime, iron magnesia, and alkalies.

These materials are quite widely distributed, though they have not been used very extensively except in Europe. They are of two classes, as regards origin: those that are the direct products of volcanic action, the material being a fine volcanic ash or dust deposited on the slopes of the volcanoes or in lakes. This group includes the more active pozzuolanic materials such as

pozzuolana proper, santorin, trass and toska. The second class includes a group of secondary materials formed from the decay of certain igneous rocks. These are much less important than the first, as they have much weaker hydraulic properties.

The pozzuolana proper is reddish brown to gray in color, insoluble in water, but partially soluble in hydrochloric acid, and has a specific gravity of from 2.3 to 2.53.

Trass, another of the natural pozzuolanas, is a volcanic tufa, being a volcanic dust which has been subjected to the action of pressure and water. This material is found in large quantities in places along the valley of the Rhine in Germany. Trass is like pozzuolana in that it contains water of hydration, and is partly soluble in hydrochloric acid and when mixed with slaked lime hardens and forms hydraulic mortar.

Santorin earth is found on the Island of Santorin and is also a kind of volcanic material. This is somewhat softer than the two preceding materials and differs from them also in its higher content of free amorphous silica and not being so easily decomposed by acids.

The following analyses of pozzuolana show fairly well its composition:*

ANALYSES OF POZZUOLANA, ITALY.

Silica (SiO ₂)	52.66	60.91	56.31	44.5
Alumina (Al ₂ O ₃)	14.33	21.28	15.23	15.0
Iron oxide (Fe ₂ O ₃)	10.33	4.76	7.11	12.0
Lime (CaO)	7.66	1.90	1.74	8.8
Magnesia (MgO)	3.86	0.00	1.36	4.7
Alkalies (K ₂ O+Na ₂ O)	4.13	10.60	11.38	5.4
Water, etc.	7.03	n. d.	6.12	9.2

“In composition trass varies between the following extremes: silica, 45 to 65 per cent.; alumina, 10 to 23 per cent.; iron oxide, 3 to 12 per cent.; lime, 1 to 8 per cent.; magnesia, 0 to 3 per cent.; alkalies, 1 to 7 per cent.; water, carbon dioxide, etc., 3 to 12 per cent.”†

*United States Geological Survey, Bull. No. 243, p. 358.

†Eckel, E. C., U. S. G. S., Bull. No. 243, p. 359.

The following is given as a typical analysis of santorin earth:

CHEMICAL ANALYSES OF TRASS AND SANTORIN EARTH.*

	I.	II.
Silica (SiO ₂)	59.75	65.55
Alumina (Al ₂ O ₃)	18.05	14.60
Iron oxide (Fe ₂ O ₃)	3.70	4.10
Lime (CaO)	1.90	3.70
Magnesia (MgO)	0.65	0.95
Loss on ignition	7.00	4.25
Alkalies, etc.	8.85	6.50
Silica soluble in caustic potash.....	17.30	14.00
Silica soluble in sodium carbonate solution.....	1.00	2.00

I. Trass.

II. Santorin Earth.

Materials very similar to the above are found in many places in the western part of the United States, but have been used but little up to the present time. Volcanic tuff deposits occur along the line of the Los Angeles aqueduct, and this material has been used in about equal volumes with Portland cement, the results being very satisfactory.

ARTIFICIAL POZZUOLANA.

Practically all of the artificial pozzuolana is manufactured from slag and in the United States especially, this has grown to be an industry of considerable importance. The slags used as a material from which to manufacture this kind of cement are the waste products of the blast furnaces smelting iron from its ores. Not all slags are of such a composition that they can be used for cement purposes, the basic ones only being of value.

The following are the specifications under which slag is accepted from the furnaces by the cement department of the Illinois Steel Company:

“(1) The slag must analyze within the following limits: SiO₂+Al₂O₃ not over 49 per cent.; Al₂O₃, from 13 to 16 per cent.; MgO, under 4 per cent.

“(2) Slag must be made in a hot furnace and must be of a light gray color.

*R. Feret, Tonindustrie Ztg. No. 15, Vol. 25. Quoted in Ohio Geol. Survey, Bull. 3, p. 42.

"(3) Slag must be thoroughly disintegrated by the action of a large stream of cold water directed against it with considerable force. This contact should be made as near the furnace as possible."*

From a series of over 300 analyses of slags used by this company in its slag cement, the following range in composition is shown: SiO_2 , 29.60 to 35.60 per cent.; Al_2O_3 and Fe_2O_3 , 12.80 to 16.80 per cent.; CaO , 47.99 to 50.48 per cent.; MgO , 2.09 to 2.81 per cent.†

The following are the requirements of the Birmingham Cement Company, as far as the chemical composition of the slags used in the manufacture of cement is concerned:

"The lime content shall not be less than 47.9 per cent.; the silica and lime together shall amount approximately to 81 per cent.; and the alumina and iron oxide together shall equal from 12 to 15 per cent."‡

These slag cements are often put on the market as Portland cements. They are not Portland cements, however, and are not well suited for all the uses for which Portland cements are adapted. Normally these cements set much more slowly than Portland cement. They are apt to contain more or less sulphur, and this has a tendency to cause disintegration, especially when the cement is exposed continually to the air.

The following is given by Eckel as showing the range in composition for a good slag cement: "The range in composition of a good slag cement may be considered to be about SiO_2 22 to 30 per cent.; $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ 11 to 16 per cent.; CaO 49 to 52 per cent.; MgO , less than 4 per cent.; S, less than 1.5 per cent.; ignition loss, 2.5 to 7.5 per cent."§

This same authority gives the following for the identification of slag cement:

"Slag cements are usually much lighter colored than the Portlands, varying from a bluish white to a light yellow. The

*Eckel, E. C., U. S. G. S., Bull. 243, p. 360.

†Eckel, E. C., U. S. G. S., Bull. 243, p. 360.

‡Eckel, E. C., U. S. G. S., Bull. 243, p. 360.

§U. S. Geol. Survey, Bull. 243, p. 369.

color of the cement depends partly upon the color of the slag and the lime, but more largely upon the relative proportions of the two ingredients.

“Cements of this class are lighter than Portlands, their specific gravity usually ranging from 2.7 to 2.8. This gives a greater bulk for the weight, but, on the other hand it reduces the density of the set cement, which is not desirable for some purposes.

“Normally, slag cements are slower setting than Portlands. Whether this property is a disadvantage or not will depend on the use to which the cement is to be applied.

“While slag cements fall below high grade Portlands in tensile strength, good American slag cements develop sufficient strength to pass the usual specifications for Portlands. Tested neat they do not approximate so closely to the Portlands as they do if tested in 2:1 or 3:1 mortars.”*

Slag cements resist very poorly mechanical wear, and hence are very poorly suited for use as surfaces of floors, pavements, etc., where this quality is of prime importance. They appear to be very well suited, however, for pavement foundations and things of this kind where a very high strength is not required.

The puzzuolana cements are said to have shown valuable properties as a material to mix with Portland cement for use in sea water. This use of this material deserves very thorough study, as it is a very important one.

The following tables show the composition of some of the slags that are being used as a material from which to manufacture cement, as well as the composition of the cements made from them:†

*Eckel, E. C., U. S. Geol. Survey, Bull. 243, pp. 370-371.

†Cement Materials and Industry of the United States, U. S. Geological Survey, Bul. 243, pp. 361, 370.

ANALYSES OF SLAG USED IN SLAG CEMENTS.

	Silica (SiO ₂)	Alumina (Al ₂ O ₃)	Iron oxides (FeO, Fe ₂ O ₃)	Lime (CaO)	Magnesia (MgO)	Lime sulphide (CaS)	Lime sulphate (CaSO ₄)	Sulphur (S)	Sulphur-trioxide (SO ₃)	CaO SiO ₂	Ratio Al ₂ O ₃ SiO ₂
1	30.00	28.00	00.75	32.75	5.25	1.90	1.09	0.93
2	31.50	18.56	42.22	3.18	0.45	2.21	1.34	.59
3	32.90	13.25	.46	47.30	1.37	3.42	1.44	.41
4	31.50	16.62	.62	46.10	1.46	.52
5	26.88	24.12	.44	45.11	1.09	1.86	1.68	.89
6	27.33	23.81	.63	45.83	.92	1.34	0.17	1.67	.87
7	26.24	24.74	.49	46.83	.88	.59	0.32	1.78	.93
8	32.20	15.50	48.14	2.27	1.49	.48
9	33.10	12.60	49.98	2.45	1.51	.38
10	31.80	14.80	49.74	2.29	1.56	.46
11	34.30	14.76	48.11	2.66	1.40	.43

1, 2. Middlesborough, England.

3. Bilbao, Spain.

4. Saulnes, France.

5, 6, 7. Choindex, Switzerland.

8, 9, 10, 11. Chicago, Ill.

ANALYSES OF SLAG CEMENTS.

	Silica (SiO ₂)	Alumina (Al ₂ O ₃)	Iron oxides (FeO, Fe ₂ O ₃)	Lime (CaO)	Magnesia (MgO)	Sulphur (S)	Sulphur-trioxide (SO ₃)	Loss on ignition
1...	19.50	17.50	n. d.	54.00	n. d.	n. d.	n. d.	n. d.
2...	30.56	13.31	0.25	45.01	2.96	(a)	(b)
3...	22.45	13.95	3.30	51.10	1.35	4.63	1.41	n. d.
4...	27.20	14.18	50.03	3.22	0.35	7.50
5...	28.40	12.80	51.50	n. d.	0.15	4.25
6...	28.95	11.40	0.54	50.29	2.96	1.40	n. d.
7...	29.80	12.30	51.14	3.34	1.37	2.39
8...	27.80	11.10	50.96	2.23	1.18	5.30
9...	27.00	12.00	55.00	n. d.	n. d.	n. d.
10...	27.78	11.70	51.71	1.39	1.31	n. d.

(a) Equals CaS.

(b) Equals CaSO₄.

1. Choindex, Switzerland.

2. Bilbao, Spain.

3. Saulnes, France.

4, 5, 6, 7, 8. Chicago, Ill.

9. North Birmingham, Ala.

10. Ensley, Ala.

RAW MATERIALS FOR NATURAL CEMENT.

Natural cements are produced by burning limestones which have had at the time of their formation more or less clayey material intimately mixed with the lime carbonate. The composition of the limestones actually used in the manufacture of natural cement varies much, the amount of clayey material contained ranging from 13 to 35 per cent. The calcium carbonate also is very variable and in some cases a considerable amount of magnesium carbonate is present.

Natural cements which carry a low percentage of argillaceous material are very closely related to hydraulic limes, while those limestones which contain a higher percentage of clay material approach more nearly the composition of the mixtures used in the manufacture of Portland cement. Natural cement differs from ordinary lime in that it will set under water and form hydraulic lime, in that it will not slake when water is added to it. It differs from Portland cement in composition, in color, specific gravity, rate of setting, and tensile strength. Natural cement usually has a yellowish or brownish color after grinding, a specific gravity from 2.7 to 3.1, sets more rapidly than Portland cement, but does not attain as high a tensile strength.

The following chemical analyses taken from Cements, Limes and Plasters, by E. C. Eckel, pp. 204-212, gives the composition of the rock from which the best known natural cements in the United States are made.

CHEMICAL ANALYSES OF NATURAL-CEMENT ROCK.

	I.	II.	III.	IV.	V.	VI.
Silica (SiO ₂)	14.15	9.69	18.33	22.07	18.52	10.66
Alumina (Al ₂ O ₃)	6.37	2.77	4.98	12.12	6.34	4.35
Iron (Fe ₂ O ₃)	2.35	1.95	1.67	3.36	2.63	1.47
Lime (CaO)	26.32	29.09	30.41	30.28	25.31	27.20
Magnesia (MgO)	12.10	15.69	8.04	2.47	12.13	16.77
Carbon dioxide (CO ₂)	34.70	40.14	32.76	} 27.60	33.31	38.81
Water	2.03		n. d.	1.53
Sulphur-trioxide (SO ₃)	1.81	0.90
Alkaline (K ₂ O, Na ₂ O)	0.18	n. d.
Cementation index ..	1.11	0.618	1.39	2.29	1.43	0.71

- I. Utica, Illinois. Average of four analyses.
 II. Louisville district, Ind.-Ky.
 III. Louisville district, Ind.-Ky.
 IV. Cumberland and Hancock, Maryland. Average of four analyses.
 V. Rosendale district, N. Y. Average of seven analyses.
 VI. Central, N. Y. Average of five analyses.

CHEMICAL ANALYSES OF NATURAL-CEMENT ROCK.

	VII.	VIII.	IX.	X.
Silica (SiO ₂)	42.0	18.34	17.28	17.30
Alumina (Al ₂ O ₃)	7.0	} 7.49	3.02	6.18
Iron oxide (Fe ₂ O ₃)	7.1		2.21	1.62
Lime (CaO)	9.91	37.60	25.11	29.54
Magnesia (MgO)	5.81	1.38	14.46	13.05
Carbon dioxide (CO ₂)	14.18	31.06	n. d.	34.17
Water and organic	14.00	3.94
Cementation index	1.49	1.18	1.18

VII. Defiance, Ohio.

VIII. Lehigh district, Pa.

IX. Millwaukee district, Wis. Average of four analyses.

X. Balcony Falls, Va. Average of two analyses.

The following analyses taken from Cements, Limes and Plasters, by E. C. Eckel, pp. 253-260, show the composition of some of the best known of the American natural cements:

ANALYSES OF NATURAL CEMENTS.

	I.	II.	III.	IV.	V.
Silica (SiO ₂)	27.60	24.16	23.32	28.02	28.30
Alumina (Al ₂ O ₃)	10.60	4.76	6.99	10.20	10.12
Iron oxide (Fe ₂ O ₃)	0.80	3.40	5.97	8.80	4.42
Lime (CaO)	33.04	46.64	53.96	44.48	49.60
Magnesia (MgO)	17.26	12.00	7.76	1.00	3.76
Alkalies (K ₂ O, Na ₂ O)	7.42
Carbon dioxide (CO ₂)	} 2.00	} 6.75	} 2.00	}	}
Water					
Cementation index	1.19	2.09	1.70

I. Utica, Illinois.

II. Louisville district, Ind.-Ky. Average of seven analyses.

III. Fort Scott, Kansas.

IV. Hancock, Md. Potomac district.

V. Cumberland, Md. Potomac district.

	VI.	VII.	VIII.	IX.	X.
Silica (SiO ₂)	27.98	28.71	17.14	26.69	25.00
Alumina (Al ₂ O ₃)	7.28	5.88	7.61	7.21	4.00
Iron oxide (Fe ₂ O ₃)	1.70	3.60	2.00	1.30	2.80
Lime (CaO)	37.59	27.00	36.83	43.12	33.40
Magnesia (MgO)	15.00	30.00	25.09	19.55	22.60
Alkalies (K ₂ O, Na ₂ O)	7.96	n. d.	3.64	1.13	2.51
Carbon dioxide (CO ₂)	} 2.49	} 3.52	} n. d.	} 1.00	} 9.50
Water					
Sulphur-trioxide (SO ₃)	1.30	n. d.	n. d.	2.59
Cementation index	0.801	1.18	1.17

VI. Rosendale district, N. Y.

VII. Rosendale district, N. Y.

VIII. Akron-Buffalo district, N. Y. "Union Akron."

IX. Akron-Buffalo district, N. Y. "Union Akron."

X. Milwaukee district, Wisconsin.

RAW MATERIALS FOR PORTLAND CEMENTS.

The essential materials for Portland cement are silica (SiO_2), alumina (Al_2O_3), and lime (CaO). Of these materials silica and alumina occur in nature in the uncombined state as minerals while lime is always combined with other substances. The most common combination is lime (CaO) and carbon dioxide (CO_2) to form calcium carbonate (CaCO_3) which occurs very abundantly as limestone. Silica (SiO_2) is very common in nature as quartz while alumina (Al_2O_3) occurs as corundum. Quartz is one of the very common rock-making minerals and as sandstone and quartzite form in places large parts of mountain ranges. Corundum is of comparatively rare occurrence in anything like large bodies. Both quartz and corundum are very hard minerals and on account of this it is almost impossible to grind them fine enough so that they will combine with the lime. In some few cases, however, quartz or finely ground sandstone in small quantities is used to make up for a deficiency of silica in the other raw materials.

Silica (SiO_2), alumina (Al_2O_3) are essential constituents of all clays, shales, and slates. They are present in greater or lesser quantity, either chemically combined or intimately mixed mechanically in these substances and the clays and shales are the principal sources of the silica and alumina that enter into the manufacture of Portland cement. Limestone (CaCO_3), of which there are a number of different varieties, is the principal source of the lime used in Portland cement manufacture.

The materials used in the manufacture of Portland cement may be separated into two general classes. The materials which contain as the principal constituent calcium carbonate would be classed as calcareous, while those in which clayey substances, as alumina and silica, are the predominating ones are classed as argillaceous. In places calcareous materials are found in nature that are practically free from impurities especially of a clayey nature. There are also clays, shales, and slates that are almost, if not entirely, free from materials of a calcareous nature. These almost pure limestones, clays, shales,

and slates, represent the extremes of the calcareous and the argillaceous groups. Between these extremes, however, are argillaceous limestones and calcareous clays, shales and slate, each group grading gradually into the other with no sharp line separating them. When the limestone contains 18 per cent. or more of silica and alumina it may be called either an argillaceous limestone or a calcareous shale, but is usually spoken of as "cement rock." In some cases certain by-products derived from other industries contain one or more of the essential constituents of Portland cement in a condition and in proportions such that the material may be used in the manufacture of Portland cement. The only important material of this class being used in the United States at present is blast furnace slag.

Grouping the materials from which Portland cement may be made into calcareous and argillaceous for the reasons given above, we have the following:*

Calcareous materials	Argillaceous materials
Limestone	Clay
Marl	Shale
Chalk	Slate
Alkali waste	Blast-furnace slag
	Cement rock†

CALCAREOUS MATERIALS.

Portland cement may be made from limestone combined or mixed with either clay, shale, slate, blast-furnace slag, or cement rock, provided the raw materials used have the required composition. This same thing is true also of marl, chalk, or alkali waste. In some localities, as the Lehigh district of Pennsylvania, Portland cement is made by burning a mixture of limestone and "cement rock" in certain proportions. In Michigan the calcareous material used is marl. This is mixed either with clay or shale and the cement usually manufactured according

*Meade, R. K., Portland Cement, p. 33.

†Cement rock varies more or less in composition, sometimes being very calcareous, while at other times it is highly argillaceous, and on account of this fact it is placed between the two groups.

to the wet or rotary process. This process consists in mixing the finely ground marl and clay or shale thoroughly in the wet condition. This mixture, which in the wet condition is known as slurry, flows into one end of a huge rotating cylinder from 40 to 170 feet long and from four or five to nine feet in diameter. The end opposite where the slurry enters is a little below the horizontal. This liquid mixture, caught on the inner side of this cylinder, gradually runs down to the lower end. Here a falling stream of crude petroleum is ignited and blown by air blasts into the end of the cylinder. A solid sheet of flame is forced into the cylinder for a considerable distance, which coming in contact with the slowly approaching slurry first dries, then heats it and by the time the lower end of the cylinder is reached, fuses it into liquid nodules about the size of small pebbles. These fall through slits in the lower end of the cylinder and are transported to the grinding machinery.

In the iron manufacturing districts of Pennsylvania and Illinois the slag from the blast furnaces is mixed with limestone and used in the manufacture of Portland cement.

The general tendency has been to use only two components in the manufacture of Portland cement, but at present in many places a three component mix is being used, as limestone, clay and shale.

The limestones are seldom absolutely pure, many foreign substances in greater or less amounts being found in them. The most common of these impurities are silica, alumina, iron and magnesia. The silica, alumina and iron occur in the limestones as clayey matter. The percentage of silica in this clayey matter is usually greater than that of the alumina and the alumina greater than that of the iron. These substances all owe their presence in the limestones to the fact that they have been carried from the land, in suspension, out to sea and deposited and become mixed with the calcareous muds of the limestones in the form of fine silt.

Cement Rocks.

The limestones which contain 20 per cent. or more of clayey material are known as "cement rock." The best known example of this is the Trenton limestone of the Lehigh district. This material is typically exposed and worked in this district, which includes Berks, Lehigh and Northampton counties in Pennsylvania, and Warren county in New Jersey. This rock forms a long narrow belt, about twenty-five miles long and not more than four miles wide in its widest place, extending in a northeasterly direction from Reading, Pennsylvania, to a few miles north of Stewartsville, New Jersey. In 1910 twenty cement plants situated in the Lehigh district of Pennsylvania were in operation and were using cement rock, while in New Jersey three plants, all located in the Lehigh district, used this material also. These twenty-three plants produced in 1910 a little more than one-third (34.3 per cent.) of all the Portland cement manufactured in the United States.

The ideal material for making a Portland cement is a rock containing about 20 per cent clayey matter and 75 per cent. of calcium carbonate. A rock having this composition might be ground and burned and made into Portland cement without the admixture of any other material. Most limestones, however, only approach this ideal composition, some being more calcareous while others are more argillaceous. To the first more clayey material would have to be added and with the last more limey material would be needed. Cement rock is usually much softer than the purest limestones that are usually used with clay or shale, and hence much more easily ground. The more nearly it approaches the required composition for Portland cement the more valuable it is.

The "cement rock" of the Lehigh district is dark gray in color with a characteristic slaty cleavage and where used in the manufacture of Portland cement ranges in composition from about 65 to 78 per cent. of calcium carbonate, about 9.5 to 22 per cent. silica, about 4.5 to 9 per cent. of alumina, about 1 to

2 per cent. of iron oxide, and about 3 to 5 per cent. of magnesium carbonate.

The following table shows the composition of the cement rock as used at various plants in the Lehigh district.*

ANALYSES OF NATURAL CEMENT ROCK USED IN THE MANUFACTURE OF PORTLAND CEMENT.

Silica	15.05	19.06	19.08	22.22	13.38	9.52	19.62	14.20
Alumina	9.02	4.44	} 7.92	7.24	} 6.08	4.72	5.58	6.14
Iron	1.27	1.14		0.92				
Lime carbonate ...	70.10	69.24	67.07	63.45	76.08	80.71	69.78	74.30
Magnesium carbonate	3.96	4.21	4.06	4.56	4.51	4.92	4.90	3.24

Pure Hard Limestones.

Under this heading are considered those limestones that have a normal hardness. This is usually made to include those limestones that have not less than 80 per cent. of calcium carbonate and have less than 5 per cent. of magnesium carbonate. Pure limestone has the composition of calcite (CaCO_3) and has 56 per cent. calcium oxide (CaO) and 44 per cent. carbon dioxide (CO_2). Limestone having this composition, however, is seldom found in nature in large quantities. The most common impurities found in limestones are silica, alumina, iron, magnesia and alkalis. The carbonate of magnesia sometimes occurs in considerable amounts in limestone and when this reaches 45 per cent. of the total carbonates the rock is known as dolomite. To be suitable for Portland cement manufacture, limestone should contain but little carbonate of magnesia, 5 per cent. being about the maximum. In some cases limestone contains more or less silica in the form of chert disseminated through it. In other cases it contains sand grains scattered through it. These are both of them detrimental to the limestone for the manufacture of Portland cement.

The limestone must be reduced to a very fine powder in order that it will intimately mix with the clay or shale used with it. On account of this the hardness of the limestone has an important bearing on its value for Portland cement making and the

*Bulletin U. S. G. S., 243, p. 289.

harder it is the more it will cost to grind it. The harder, more dense and crystalline the limestone is, the slower will the carbon dioxide be evolved and hence a greater expense incurred in the burning of the cement.

The following table shows the composition of some of the pure hard limestones that are being used in the manufacture of Portland cements in various parts of the United States:*

ANALYSES OF HARD LIMESTONES USED AT AMERICAN PORTLAND CEMENT PLANTS.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Silica (SiO ₂)	1.21	2.12	5.43	1.00	0.89	0.40	0.06	3.30
Alumina (Al ₂ O ₃)	0.70	0.28	1.43	0.90	0.38	0.44	0.03	1.30
Iron oxide (Fe ₂ O ₃)	0.50	0.50		2.00	0.25		1.03	
Lime (CaO)	53.62	54.06	52.02	51.10	54.43	54.87	53.86	52.15
Magnesia (MgO)	0.44	0.77	1.11	1.40	0.36	0.20	1.53
Carbon dioxide (CO ₂)	42.98	42.34	40.24	43.50	43.40	43.34	43.20	40.98
Water (H ₂ O)								
Sulphur-trioxide (SO ₃) ...	0.11	0.30

- I. Pacific P. C. Co., Suisun, California.
- II. Southern States P. C. Co., Rockmart, Ga.
- III. German-American P. C. Works, LaSalle, Ill.
- IV. Iola P. C. Co., Iola, Kansas.
- V. Bedford P. C. Co., Bedford, Ind.
- VI. Atlas P. C. Co., Iasco, Mo.
- VII. Ironton P. C. Co., Ironton, Ohio.
- VIII. Glens Falls P. C. Co., Glens Falls, N. Y.

Chalk.

Chalk, strictly speaking, is carbonate of lime and consists of the remains of the shells of marine animals, among which the microscopic forms, known as foraminifera, are abundant. Chalk is a soft somewhat loosely coherent substance and when free from impurities is white in color. Like other calcareous deposits, however, it often contains various impurities and on account of these may vary somewhat in color. The chalks are usually considerably lighter in weight than the hard limestones. They are usually very porous and capable of absorbing a large amount of moisture and only a very brief exposure to water may increase their weight very materially. The fact that chalk is soft and

*Eckel, Cements, Limes and Plasters, p. 314.

easily quarried and ground makes it a valuable material for use in the manufacture of Portland cement.

In composition chalks vary from those that are almost pure calcium carbonate with only very small amounts of magnesia and of clayey material to an impure clayey limestone. Magnesia is not apt to be found in them in large amounts, but some other substances such as alkalis and sulphur may occur in considerable quantities.

The following table shows the composition of some of the chalks that are being used in American Portland Cement Plants:

ANALYSES OF CHALK USED IN THE MANUFACTURE OF PORTLAND CEMENT.

	I.	II.	III.	IV.	V.
Silica (SiO ₂)	4.42	6.09	3.83	5.77	5.94
Alumina (Al ₂ O ₃)	2.21	3.52	2.31	} 2.14	1.72
Iron oxide (Fe ₂ O ₃)	1.03	1.20		
Lime (CaO)	53.36	49.24	52.16	50.45	48.73
Magnesia (MgO)	0.14	0.28
Carbon dioxide (CO ₂)	41.93	38.69	41.64	40.00	86.57
Water (H ₂ O)	3.81
Sulphur-trioxide (SO ₃)	0.20

I.-II. Whitecliffs P. C. Co., Whitecliffs, Ark. Trans. A. I. M. E., Vol. 27, p. 58.

III. Western P. C. Co., Yankton, S. Dak. Bulletin U. S. G. S. No. 243, p. 301.

IV.-V. Alamo Cement Works, San Antonio, Tex. 22nd Ann. Report U. S. Geol. Survey, pt. 3, p. 737.

Fresh-Water Marls.

Marls, at least in the sense in which the term is used in the Portland cement industry, are friable, fine-frained limestones which occupy either extinct or existing lakes. Chemically, marls are usually quite pure limestones, being composed almost entirely of carbonate of lime. They differ mainly from the hard compact rock to which the term limestone is commonly applied, in being granular, loose, soft uncompact masses of sediment. Marls vary more or less in composition on account of the conditions under which they have been formed having been somewhat different. The deposits in some cases cover only very

small areas while in others they cover hundreds of acres and have an average thickness of as much as twenty feet.

Pure marl is white in color, but it is seldom found free from impurities of various kinds, such as organic material, sand, and clayey material. This organic matter gives to it a grayish or yellowish cast and if the amount is very large the color will be very dark gray. Marl as found either in existing lakes or in swamps or marshes carries a considerable amount of water. On account of this water and the fine granular condition of the marl it is somewhat sticky and plastic in character.

Of the impurities mentioned above as occurring in the marls, the organic matter is perhaps the most objectionable as far as the use of the marl in the manufacture of Portland cement is concerned. A small amount of organic matter would have little effect, but a large amount would be objectionable because it would lower relatively the amount of calcium carbonate in any given amount of marl and because it holds water with very great tenacity. Marl containing much organic matter is dried only with the greatest difficulty and if the dry or semi-dry process is to be used in the manufacture of the Portland cement this would be a serious disadvantage, as it would require a large amount of fuel and hence entail additional expense. Sand is not usually present in very large amounts and what does occur is usually in quite fine particles and will have very little effect on the cost of grinding. Clays are apt to contain magnesia and if they occur in a marl in very large amounts they may make the marl unfit for use in making Portland cement.

The marls vary somewhat in texture not only in different deposits but also in different parts of the same deposit. The cost of pulverizing, however, is comparatively low and is a point in their favor.

The following table, in which all analyses are calculated dry, all water below 212 degrees being neglected, shows the composition of the marls used at some of the American Portland cement plants:

ANALYSES OF MARLS USED IN THE MANUFACTURE OF PORTLAND CEMENT.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Silica (SiO ₂)	1.74	3.80	0.19	0.22	1.24	1.19	6.22	1.98
Alumina (Al ₂ O ₃)	0.90	n. d.	0.05	} 0.76	0.80	0.55	1.70	} 0.97
Iron oxide (Fe ₂ O ₃)	0.28	n. d.	0.07		0.25	0.86		
Lime (CaO)	49.84	51.10	51.31	51.56	50.90	52.50	47.86	50.95
Magnesia (MgO)	1.75	1.54	1.98	1.26	1.43	1.16	0.04	0.55
Alkalies (K ₂ O, Na ₂ O)						1.84	2.20	0.12
Sulphur-trioxide (SO ₂)	1.12	0.24	0.14			tr.		0.10
Carbon dioxide (CO ₂)	} 46.01	41.82	42.40	} 46.20	41.54	42.51	42.11	40.03
Organic matter		1.50	2.25		4.09	n. d.		0.25

- I. Sandusky P. C. Co., Syracuse, Ind. 25th Ann. Rept. Indiana Dept. Geology, p. 29.
- II-III. Millens P. C. Works, South Bend, Ind. 25th Ann. Rept. Indiana Dept. Geology, pp. 25, 273.
- IV. Peninsular P. C. Co., Cement City, Michigan. Vol. 8, Michigan Geological Survey, p. 236.
- V. Newaygo P. C. Co., Newaygo, Mich. Vol. 8, Michigan Geological Survey, p. 240.
- VI. Wolverine P. C. Co., Coldwater, Michigan. Vol. 8, Michigan Geological Survey, p. 247.
- VII. Montezuma, N. Y. Mineral Industry, Vol. 1, p. 52.
- VIII. Buckeye P. C. Co., Harper, Ohio. Mineral Industry, p. 52.

Alkali Waste.

Alkali waste, as the term implies, is the waste or by-product in the manufacture of certain alkalies, especially caustic soda. This consists very largely of carbonate of lime in a soft fine grained condition and if it is free from injurious impurities it furnishes a cheap source of lime for use in the manufacture of Portland cement. It has been used at but one plant in the United States so far and there appears to be very little probability of this ever becoming an important source of supply for material from which to manufacture cement.

ARGILLACEOUS MATERIALS.

Under the head of argillaceous materials are included all of those substances that furnish the silica, alumina and iron oxide to the cement mixture and are clay, shale, slate, and blast furnace slag. The clay, shale and slate are of practically the same composition, but differ in their degree of consolidation. They have all of them been derived originally from the decay of older rocks, the fine particles resulting from this decay having been carried by the streams and deposited either along their courses or in the ocean or some other body of water into which the

stream empties. All of the representatives of this group of materials consist essentially of silica and alumina with usually iron calcium, magnesium, and alkalis in varying amounts.

Clays.

The clays vary much as regards the manner of their formation, but if classified according to their origin they fall into a number of groups the most important of which, when considered as materials to be used in the manufacture of Portland cement, are transported, residual, and glacial. The transported clays are the most important of these different classes.

The silica in the clay exists either chemically combined or in the free state. In the latter it is in the form of grains of sand or nodules of flint and quartz. If the free silica is in a very finely divided condition it may not be detrimental, provided, however, that it is not present in too large an amount. If coarse grains of sand occur, these must be finely ground so that they will unite with the lime in burning. This is necessary because free silica will unite with lime, at the temperature obtained in the cement kiln, only when in very fine particles.

Some clays contain considerable amounts of the micas, some of which contain magnesia and should they occur in any very large amounts in the clay they might be the means of introducing into the cement mixture undesirable amounts of magnesia and alkalis.

Many clays contain more or less particles of the feldspars which are silicates of alumina with potash, soda or lime. The alkalis act as powerful fluxes and would cause the clay with which they occur to fuse at lower temperatures than it would if they were not present.

The feldspars in clay, where it is to be used in the manufacture of cement, would reduce the temperature at which the combinations with the lime would take place in the kiln. From this standpoint the feldspars would be desirable constituents of the clays. They also bring in a smaller amount of alumina in proportion to the silica than does the clay substances proper, one part of silica in the case of the orthoclase introducing only

0.284 of one part of alumina. From this standpoint also, the feldspars would be beneficial.

Where the amount of feldspar is large there would be a considerable amount of the alkalis, potash and soda introduced into the cement mixture and there appears to be some difference of opinion as to just what effect this would have on the cement. Eckel makes the following statement in regard to alkalis in Portland cement:*

“If the total amount of alkalis is above 5 per cent., however, a sufficient amount will be carried over into the cement to cause trouble; and raw materials carrying more than 5 per cent. of soda and potash together should therefore be looked upon with suspicion, if not absolutely rejected.”

The following is from Practical Cement Testing by Taylor:†

“Alkalis (K_2O and Na_2O) appear to have but little influence on either the burning or quality of the cement. It has been held that alkalis acted more or less as a flux in facilitating the combination of lime with the silica and alumina, but later experiments have apparently disproved this theory. Excess of alkalis, under certain conditions, is said to be responsible for unsoundness, although this fact has never been definitely proven. The percentage of alkalis is usually from 0.5 to 2 per cent.”

Bleiningger makes the following statement in regard to the addition of feldspar:‡

“The clinkering temperature was reduced by the addition of even small amounts of feldspar and the cements produced were of normal setting qualities.”

Iron Oxide—Iron oxide is a very common constituent of many of the clays. It may vary in amount from a trace to as high as 32 per cent. The color of many of the clays is due to the iron they contain. The oxides usually found in the clays are hematite (Fe_2O_3) and limonite ($Fe_2O_3, 3 H_2O$). The igneous rocks from which the clays are formed contain more or less of the iron-bearing minerals and when these decompose these minerals are oxidized to form hematite and limonite.

*Cements, Limes and Plasters, p. 310.

†Practical Cement Testing, p. 11.

‡Geological Survey of Ohio (4th Series) Bull. No. 3, p. 66.

According to some authorities ferric oxide and calcium carbonate on burning yield products which slake with water and possess no hydraulic properties. Others have prepared cements in which the alumina has been entirely replaced by iron and hence have concluded that the function of these two substances is exactly the same. The investigations of the Newberry brothers show that ferric oxide and alumina are practically identical in promoting the union of silica and lime.

The amount of these iron oxides present in the clays used in the manufacture of Portland cement is usually small, so that the principal thing they do is to color it.

Iron Sulphide—Iron sulphide is found in many clays as pyrite or marcasite (FeS_2), especially where the clays have not been subjected to weathering agencies. The pyrite is brass yellow in color while the marcasite is pale yellow. They occur in small crystals disseminated through the beds, in nodules, or in aggregates of crystals. These sulphides, however, on exposure to the atmospheric agencies, slowly oxidize and form ferrous sulphate (FeSO_4). This is readily soluble and if the clay has been subjected to the leaching action of water the iron will be more or less completely removed.

The amount of the sulphides of iron in clays is usually very small, so that they probably have very little effect except to color the cement. Should they occur in large amounts, however, as the sulphides, they might introduce an injurious amount of sulphur.

Calcite—Many clays contain calcium carbonate, some of them having a large amount. The calcium is an essential constituent in the manufacture of Portland cement and hence a clay containing it would not be injured for this purpose by it.

Gypsum—Gypsum, which is the hydrous calcium sulphat ($\text{CaSO}_4, 2\text{H}_2\text{O}$), is also found in some clays. Small amounts of this would not be injurious to the clay. The effect of calcium sulphat on Portland cement is to delay the set and in small amounts is beneficial. More than four or five per cent. in the cement is generally considered harmful.

Magnesia—Many clays contain more or less magnesia. It may occur either as a sulphate ($MgSO_4$) or as the carbonate ($MgCO_3$). As the carbonate it is probably usually combined with calcium carbonate ($CaCO_3$ $MgCO_3$). Clays containing any large amount of magnesia are usually considered unsuitable for use in the manufacture of Portland cement. While at the present time there is some differences of opinion as to what effect a considerable amount of magnesia has on Portland cement, the standard specifications place the maximum amount of magnesia (MgO) at 5 per cent. Ordinarily the amount in clays is not larger than this and does not prevent them from being used in the manufacture of Portland cement.

A clay to be of value for use in the manufacture of Portland cement should be homogeneous in texture, fine-grained and of correct and uniform composition throughout. It should contain at least 55 per cent., and preferably between 60 and 70 per cent. of silica. The alumina and iron oxide together may range from about two-sevenths to not more than one-half the percentage of silica and the composition will usually be better the nearer the percentage ratio $\frac{SiO_2}{Al_2O_3 + Fe_2O_3} = 3$ is approached.

The amount of alkalis should be low and ordinarily the amount of iron should not be more than about one-third the amount of the aluminium. Below are given a few analyses of clays that are being used in Portland cement manufacture:

ANALYSES OF CLAYS USED IN AMERICAN PORTLAND CEMENT PLANTS.

	I.	II.	III.	IV.	V.	VI.
Silica (SiO_2)	61.92	63.73	57.25	58.25	62.50	64.88
Alumina (Al_2O_3)	16.58	22.12	} 26.15	18.56	20.20	17.98
Iron oxide (Fe_2O_3)	7.84	9.01		7.35	7.50	5.92
Lime (CaO)	2.01	2.83	3.09	3.10	0.80	2.24
Magnesia (MgO)	1.58	1.10	1.28	1.80	1.40
Alkalis (K_2O , Na_2O)	3.64	0.21	1.88	2.35	n. d.	n. d.
Sulphur-trioxide (SO_3)	tr.	n. d.	0.39	0.45	0.40	n. d.
Carbon-dioxide (CO_2)	n. d.	n. d.	} 9.30	8.55	n. d.	4.98
Water (H_2O)	n. d.	n. d.				
SiO_2 }	2.53	2.04	2.19	2.25	2.26	2.82
$Al_2O_3 + Fe_2O_3$ }						

- I. Catskill P. C. Co., Smiths Landing, N. Y.
 II. Santa Cruz, Calif. Mineral Industry, Vol. 1, p. 52.
 III-IV. Pacific P. C. Co., Suisun, Calif. C. J. Wheeler, analyst.
 V. Iroquois P. C. Co., Caledonia, N. Y.
 VI. Omega P. C. Co., Janesville, Mich. Vol. 8, Michigan Geological Survey, p. 229.

Shales.

Geologically, clays and shales are very similar, shales being consolidated clays which have been deposited in comparatively still water and hardened by pressure and given their characteristic structure and cleavage. By heat and pressure these shales are metamorphosed or changed to form slates. The shales like the clays vary much in chemical composition and may fuse readily or be very refractory. Based on composition we may have silicious shales, aluminous shales, ferruginous shales, calcareous shales, and carbonaceous shales.

Silicious Shales—These are shales which contain more than an average amount of silica. In some cases transitions of shales to sandstones occur, in which the percentage of silica gradually increases as the sandstone is approached. When this silica occurs in a very finely divided condition these shales may be valuable in the manufacture of Portland cement.

Aluminous Shales—Shales of this character may be formed by the hardening and taking on of a shaley structure of kaoline, fire clay, or any clay high in alumina. These shales would be undesirable in the manufacture of Portland cement on account of the high percentage of alumina making a very quick setting cement, unfit for use. The cost of manufacture would be increased unnecessarily on account of the high temperature at which they would have to be burned.

Ferruginous Shales—Shales carrying a high percentage of ferric oxide are common in many localities and in many cases are sources of valuable cement material. Shales, on account of being very fine grained and uniform in composition, are especially desirable materials from which to manufacture cement, especially if they have been weathered and at least partially decomposed. One of the principal advantages that a shale high in iron has is the low temperature at which it will fuse and shales high in iron are to be preferred to clays low in iron and higher in alumina. The cement made from these shales would of course be dark colored on account of the high iron content. The dark

color, however, is the only objection that can be made against the cement.

Some shales contain iron in the form of nodules or concretions disseminated through them. These vary much in size and range from those that are an inch in diameter to those that are as much as six inches in diameter. When these cannot be removed they make the shale worthless.

Ferringinous shales, if they do not contain too much alumina and magnesia, are not too hard, and they are comparatively free from concretionary iron, are desirable materials from which to manufacture cement. The limit of the ferric oxide content is usually placed at about ten per cent.

Calcareous Shales—Many shales carry a considerable amount of calcium carbonate and as calcium is one of the essentials of Portland cement these shales may be valuable materials for use in its manufacture. Shales of this character are most likely to occur in connection with limestones or highly calcareous materials and in fact more or less impure limestones often weather into shales.

Carbonaceous Shales—These are shales that contain more or less carbonaceous material. These shales are usually black in color, unless they have been weathered, when they are often reddish or yellowish. The organic matter in these shales may be beneficial, as it may aid in the burning of the cement.

The following analyses show the chemical composition of some of the shales that are being used in the manufacture of Portland cement:

ANALYSES OF NORMAL SHALES USED IN AMERICAN CEMENT PLANTS.

	Silica (SiO ₂)	Alumina (Al ₂ O ₃)	Iron oxide (Fe ₂ O ₃)	Lime (CaO)	Magnesia (MgO)	Alkalies (K ₂ O, Na ₂ O)	Sulphur-trioxide (SO ₃)	Carbon dioxide (CO ₂)	Water (H ₂ O)	SiO ₂ Al ₂ O ₃ +Fe ₂ O ₃
1.....	57.98	18.26	4.57	1.75	1.83	n. d.	1.28	12.08		2.5
2.....	65.99	21.57	6.07	0.47	0.82	n. d.	n. d.	n. d.	n. d.	2.4
3.....	60.00	23.26	4.32	0.90	1.12	n. d.	n. d.	n. d.	n. d.	2.2
4.....	69.49	16.42		2.29	0.78	n. d.	n. d.	5.43	n. d.	4.2
5.....	55.00	21.79	9.26	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	1.4
6.....	70.20	26.90		n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	2.6
7.....	57.82	21.76		8.32	1.81	n. d.	n. d.	n. d.	n. d.	2.6
8.....	60.02	26.60		2.31	1.62	n. d.	n. d.	n. d.	n. d.	2.6
9.....	61.09	19.19	6.78	2.51	0.65	3.16	1.42	5.13		2.4
10.....	61.15	18.47	5.05	0.98	2.26	n. d.	0.91	7.02		2.6
11.....	58.24	18.56	7.68	0.61	0.24	n. d.	n. d.	10.04		2.2
12.....	59.64	19.14	7.59	0.26	2.31	4.33	n. d.	4.71		2.2
13.....	68.62	12.68	4.20	1.31	1.79	3.73	3.00	4.47	4.1
14.....	53.63	24.47		5.94	1.79	10.63		2.2
15.....	58.07	19.08	6.16	none	0.64	11.17		2.3

- Western P. C. Co., Yankton, S. D. Mineral Industry, Vol. 6, p. 97.
- Crescent P. C. Co., Wampum, Pa. U. S. Geol. Survey, Bull. 243, p. 294.
- Ivanton P. C. Co. C. D. Quick, analyst. U. S. Geol. Survey, Bull. 243, p. 274.
- Alma P. C. Co. Twenty-first Ann. Rept. U. S. Geol. Survey, pt. 6 (continued), p. 402.
- Diamond P. C. Co. E. Davidson, analyst. U. S. Geol. Survey, Bull. 243, p. 274.
- Hudson P. C. Co., Hudson, N. Y. Cements, Limes, and Plasters, p. 357.
- 7-8. Cayuga P. C. Co., Portland Point, N. Y. U. S. Geol. Survey, Bull. 243, p. 261.
- Alpena P. C. Co., Coldwater, Mich. Vol. 8, pt. 3, Reports Mich. Geological Survey, p. 227.
- Wolverine P. C. Co., Coldwater, Mich. Cements, Limes, and Plasters, p. 357.
- Michigan P. C. Co., Coldwater Mich. Cement Industry, p. 78.
- Lehigh P. C. Co., Mitchell, Ind. 26th Ann. Report Indiana Dept. Geol., p. 276.
- East Bangor, Pa. Twentieth Ann. Report U. S. Geol. Survey, pt. 6 (continued), p. 436.
- Virginia P. C. Co., Craigsville, Va. Virginia Geol. Survey, Bull. No. II. A, p. 266.
- Near Craigsville, Va. Virginia Geol. Survey, Bull. No. II. A, p. 266.

The following chemical analyses show the composition of some of the more limy shales that are being used in the manufacture of Portland cement:

ANALYSES OF LIMEY SHALES USED IN AMERICAN CEMENT PLANTS.

	Silica (SiO ₂)	Alumina (Al ₂ O ₃)	Iron oxide (Fe ₂ O ₃)	Lime (CaO)	Magnesia (MgO)	Sulphur-trioxide (SO ₃)	Carbon dioxide (CO ₂)	Water (H ₂ O)	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$
I.	53.17	20.60	4.09	4.02	2.24	n. d.	13.70		2.1
II.	52.74	21.73		12.37	2.01	n. d.	12.27	n. d.	2.4
III.	54.18	19.17	6.11	7.05	1.89	n. d.	11.95		2.1
IV.	56.00	22.10		8.00	1.50	tr.	10.70		2.5
V.	57.45	20.56	2.78	4.27	3.17	0.35	8.15		2.4
VI.	56.64	12.18	3.59	8.17	4.29	0.31	n. d.	n. d.	3.5
VII.	57.82	21.76		8.32	1.81	n. d.	n. d.	n. d.	2.6
VIII.	38.84	17.76		21.58	1.78	n. d.	n. d.	n. d.	2.1
IX.	50.48	8.89		23.74	2.21	n. d.	n. d.	n. d.	5.68
X.	46.54	21.50		11.51	1.88	n. d.	n. d.	n. d.	2.1

- I. Chicago P. C. Co., Oglesby, Ill. U. S. Geol. Survey, Bull. 243, p. 136.
 II. German-American P. C. Works, LaSalle, Ill. U. S. Geological Survey Bull. 243, p. 136.
 III. Iola P. C. Co., Iola, Kansas. U. S. Geol. Survey, Bull. 243, p. 170.
 IV. Kansas P. C. Co., Iola, Kansas. U. S. Geol. Survey, Bull. 243, p. 170.
 V. Alpena P. C. Co., Alpena, Michigan. Cements, Limes, and Plasters, p. 359.
 VI. Bronson P. C. Co., Bronson, Mich. Cements, Limes, and Plasters, p. 359.
 VII-X. Cayuga P. C. Co., Portland Point, N. Y. Cements, Limes and Plasters, p. 359.

CHAPTER III.

COMPOSITION AND ORIGIN OF LIMESTONES, CLAYS AND SHALES.

The raw materials used in the manufacture of the different kinds of cements, are limestone, clay, shale, marl, chalk, slag and pozzuolana. Each of these materials, with the exception of the last, is used in some part of the United States in the manufacture of the different classes of cement. In Washington, however, only the hard limestone, shale and clay are being used for this purpose. On account of the very great importance of the Portland cement industry and the fact that limestones, clays and shales are used so extensively in the manufacture of Portland cement, a fairly complete discussion of the origin, composition, and general characters of these different substances will be given.

LIMESTONE.

CHEMICAL COMPOSITION.

The term limestone as generally used is made to include a large group of rocks which vary considerably in composition, texture, color and origin, and having but the one property in common, that of consisting essentially of carbonate of lime. The most important of these are calcite, dolomite, marl, travertine, calcareous sinter, and chalk. A pure limestone should be composed entirely of calcium carbonate and would be pure white. As a matter of fact, however, very little if any of our natural limestone is chemically pure. The foreign material occurring in the limestone is either combined chemically or mixed mechanically with the calcium carbonate. The most common of these foreign substances are carbonate of magnesia, carbonates and oxides of iron, silica, clay, and bituminous matter. The presence of these substances gives rise to a variety of colors such as pink, red, blue, gray of various shades, and black. The pink and red colors are usually due to iron oxides, while the blue

and gray colors are due to the carbonaceous matter which has been derived from the decay of organic remains.

Limestone is a carbonate of lime (Ca CO_3) and theoretically has 56 parts by weight of the oxide of the metal calcium (CaO) combined with 44 parts by weight of carbon dioxide (CO_2). Limestones as a general rule are quite soft, being easily scratched with a knife and will effervesce when treated with cold dilute acids.

MINERALOGICAL COMPOSITION.

The different elements occurring in nature have the power of combining or uniting with each other in definite fixed proportions and it is this union or combination that produces what we know as minerals. Limestone is composed essentially of one or more of the minerals calcite, aragonite, or dolomite. Calcite is the most common of these three and also one of the most common of all minerals. Calcite is composed principally of calcium carbonate (Ca CO_3) but may contain small amounts of other substances, the most common of which are magnesium, iron and manganese. The hardness of pure calcite crystals is usually given as three, but this will vary somewhat for certain reasons.

The specific gravity of pure calcite crystals is from about 2.713 to 2.723. The impure varieties, however, will vary much. Calcite when pure is white or colorless, but is found with various colors, such as pale shades of gray, red, green, blue, violet and yellow. It has well marked cleavage in three directions which causes it to split readily in these directions and to form rhombohedral blocks.

Aragonite has the same composition as calcite, but differs in its physical properties. It is harder than calcite, being from three and one-half to four. The ordinary variety has a specific gravity ranging from 2.927 to 2.947, while certain inferior varieties are higher than this.

Dolomite in composition is unlike the two preceding minerals, in that it is a double carbonate of calcium and magnesium ($\text{CaCO}_3\text{Mg CO}_3$) and for a normal dolomite

should contain carbon dioxide (CO_2) 47.9 per cent.; lime (CaO) 30.4 per cent., magnesia (MgO) 21.7 per cent., or calcium carbonate (Ca CO_3) 54.35 per cent., and magnesium carbonate (Mg CO_3) 45.65 per cent. The carbonates of calcium and of magnesium in a normal dolomite are in the ratio of one molecule of calcium to one molecule of magnesium, but dolomites occur in which other proportions are found and, in fact, there are cases where the amount of magnesium is very small but in such cases they are hardly dolomites, but rather magnesian calcites. In some cases a part of the calcium carbonate or a part of the magnesium carbonate, or of both, have been replaced by iron and we have a ferriferous dolomite; in other instances manganese carbonates occur and we have manganiferous dolomite which is colorless to flesh-red.

Dolomite is distinguished from calcite by its hardness, its specific gravity, and by the fact that it does not effervesce when treated with cold dilute acids. It will, however, frequently take a chemical analysis to determine with certainty whether it is a dolomite or not.

ORIGIN OF LIMESTONES.

Two widely differing views are held in regard to the manner of formation of the limestones. By some it is held that the larger part of the limestone deposits have been formed through the accumulations in the ocean of the remains of marine forms, while by others they are thought to have been formed mainly as the result of chemical precipitation from sea water without the intervention of organic agencies. The larger deposits of limestones are probably in most cases the results of organisms of some kind. In many cases the deposits still show the shells and skeletons of such forms as the corals, crinoids, mollusks and others. In many cases these shells have become thoroughly comminuted to calcareous slime before final deposition and then the resulting rock shows no traces of organic structure.

Materials obtained from the deeper portions of the continental platform show that a considerable part of the unconsol-

idated deposits that occur there are composed of the calcareous remains of small animals. These accumulations form extensive deposits, which, when they are consolidated, should form beds of limestone. In many cases, at least, where the shells and skeletons of animals form a considerable part of a deposit, chemical action has been a very important agency in consolidating the deposit.

Pure water, when brought in contact with the different minerals and rocks composing the crust of the earth, has very little effect on them, but as a matter of fact we have no absolutely pure water in nature. Rain water, which is the purest water we have, absorbs carbon dioxide as it falls through the atmosphere and when it reaches the earth it is very apt to be brought more or less in contact with decaying organic matter and in this way it will receive more or less of the organic acids. As this water, containing carbon dioxide and organic acids slowly circulates through the crust of the earth, it comes in contact with the different rocks and minerals and those that are soluble are slowly taken into solution. If this water should come in contact with limestone the dissolving of it would set free more carbon dioxide, which would be absorbed by the water and this might continue until the water would become saturated. As this underground water issues in caves or on the surface as springs, it is not subjected to so great pressure and some of the carbon dioxide escapes, calcium carbonate is deposited, if in caves as stalactites or stalagmites, and if along streams or around springs as travertine, calcareous sinter, or tufa. The depositing of the calcium carbonate in the above cases is due partly to the decrease of pressure and escape of the carbon dioxide and partly to the evaporation of the water.

IMPURITIES IN LIMESTONES.

Silica.

Silica may occur in limestones either in the free or in the combined state. In the free state it may occur as sand in small grains or as chert in nodules. The percentage of these substances may vary from a fraction of a per cent. to almost all

silica. As the amount of sand increases but is still subordinate to the calcite, the stone is spoken of as a siliceous limestone, but when the percentage of sand has increased so that it predominates, then it is known as a calcareous sandstone. When the percentage of sand is high the stone would not be suitable for a Portland cement material. In many cases the chert in the form of nodules may be readily separated from the limestone and would have no detrimental effect except to increase the cost of the raw material. Where the chert cannot be easily separated from the limestone or where the percentage of chert is large, the stone would be unsuited as a material from which to manufacture lime or cement.

In the combined state silica occurs in the form of clay more often than in any other way. This is more especially true in the case of the unaltered limestones. In the metamorphosed limestones other silicates are more likely to occur. Clay is a very common impurity and but few limestones are entirely free from it. All gradations are found, from a limestone which is practically free from clay to one in which the clay is by far the most important constituent of it. Those limestones in which the clay is in considerable amount, but still is not the predominating constituent, are known as argillaceous limestone, but when the clay becomes the predominating substance the rock is designated as calcareous shale. For some purposes clay is an essential constituent rather than an impurity in a limestone. In the manufacture of lime, any considerable amount of clay would be detrimental, while for natural cement the clay is absolutely necessary and the value of the limestone for this purpose is due to the presence of the clay.

Iron.

Iron is present in the larger part of the limestones. Usually, however, it occurs only in small quantities. Iron occurs in the limestones generally in the form of the oxide, the carbonate, or the sulphide. In some cases the amount of iron present is due partly at least to secondary enrichment due to circulating water. The oxides hematite and limonite are often the cause

of the brown and buff colors of many limestones. The carbonate of iron is often found disseminated through limestone deposits and is the cause of the bluish gray color. The disulphides pyrite and marcasite are also found disseminated through many limestone deposits as small yellow particles. The sulphides would be a source of sulphur and would injure the limestone for the manufacture of cement, while the iron from any of the iron minerals would injure the limestone where a white lime is desired.

Alumina.

This substance when found in limestone is almost invariably in the form of clay and will be treated under this subject.

Organic Matter.

Many limestones contain more or less organic matter. This, however, has but little, if any, effect on the value of the stone.

Alkalies.

The alkalies soda and potash are sometimes present in small amounts in limestone. These in all probability occur in the form of carbonates. They are rarely present, however, in sufficient quantity to effect the value of the limestone.

Sulphur.

Sulphur is often present in limestones and may occur either as iron disulphide (FeS_2) pyrite or marcasite, or as gypsum or lime sulphate ($\text{Ca SO}_4 + 2 \text{H}_2\text{O}$).

Resume.

The impurities described above may all of them be present in the same limestone and the percentage of these as a whole, and the relative proportion of each will determine very largely the use for which any stone would be suited. The texture and hardness will also help determine the value of a given stone for a certain purpose. Those limestones that have an open porous structure would be more easily ground to a fine powder than the hard compact ones and hence would be more valuable for certain purposes.

MARLS.

The term marl has been used to include materials which vary quite widely in composition and conditions under which they formed. As already stated, the term is used in the Portland cement industry at the present time, to apply only to those fine-grained friable limestones which have been deposited in the basins of existing or extinct lakes. From the standpoint of composition, marls are almost pure limestones (Ca CO_3). Physically they differ very much from those hard compact rocks to which the term limestone is usually applied. On account of the conditions under which the marls have formed, they consist of loose, granular, uncompacted deposits.

In parts of the United States these marls are being extensively used as materials from which to manufacture Portland cement.

TRAVERTINE AND CALCAREOUS SINTER.

These are forms of calcium carbonate that have been deposited from solutions around the vents of springs, by percolating waters in caverns, or in lakes and streams. The deposits are often very pure, usually white, and somewhat translucent, though they may be colored by small amounts of other substances that have been dissolved and redeposited with the lime. Deposits of these materials are of very local occurrence and are not of especial commercial importance.

CHALK.

Chalk is a white earthy limestone which is so soft as to be easily marked with the finger nail. It is composed of the remains of marine mollusks in a finely comminuted condition along with large numbers of microscopic forms known as foraminifera. When pure its chemical composition is mainly calcium carbonate.

CLAY AND SHALE.

Theoretically, the basis of all clays is kaolinite, a hydrous aluminum silicate represented by the formula $\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$. In addition to kaolinite, other substances occur in

greater or lesser amounts and clay deposits which approach closely the theoretical composition of kaolinite are comparatively scarce. The materials included under the term clay vary much in composition, physical properties, and color.

Shale is a clay that has been hardened somewhat largely by means of pressure. Shales have been deposited under water, are well stratified, and contain more or less of the impurities that were deposited with the kaolinite. Where shales have been subjected to certain forces they are metamorphosed or changed to slates. This change does not affect the chemical composition and a shale or slate should have the same composition as the clay from which it was formed.

ORIGIN OF CLAYS.

Clays are secondary products that have been derived from the decomposition of various kinds of rocks. As stated above, the basis of all clay is kaolinite and the rocks from which the clays have been derived must have contained minerals from which the kaolinite would form when they decomposed. The most common of these minerals are the feldspars. These are all double silicates and are silicates of alumina with either potash, soda or lime or mixtures of these.

Taking orthoclase as the typical feldspar, we find it has the formula $K_2O, Al_2O_3, 6 SiO_2$, with the following percentage of each of these substances:

Silica (SiO_2)	64.7 per cent.
Alumina (Al_2O_3)	18.4 per cent.
Potash (K_2O)	16.9 per cent.

Kaolin has the formula $Al_2O_3, 2 SiO_2, 2 H_2O$, with the percentage composition as follows:

Silica (SiO_2)	46.5 per cent.
Alumina (Al_2O_3)	39.5 per cent.
Water (H_2O)	14.0 per cent.

The feldspar is a potash aluminum silicate while kaolin is a hydrous aluminum silicate. The changes that have taken place in the feldspar to form kaolin have been the removal of the potash, a decrease in the percentage of silica, and the addition of a certain amount of chemically combined water. The

most noticeable physical change is in the transforming of a hard crystalline substance to one that is soft in character.

The mineralogical composition of the igneous rocks varies much, but the larger part of them contain in greater or lesser amounts aluminum silicate minerals which when they decompose will produce clay.

Granite, as an illustration, is composed mainly of quartz, feldspar, and mica or hornblende. In addition to the above named minerals, small amounts of others such as magnetite, apatite and augite are present. When this rock is exposed on the surface of the earth to the atmospheric agencies, they begin to decompose it. The first of these minerals to be affected is the feldspar, which gradually changes color more or less, the potash, soda, or lime being gradually taken into solution, removed and water added. While the feldspar is being dissolved, the other minerals are being affected more or less also. The mineral to be most affected after the feldspar is the hornblende. This, however, is more complex in its composition than the feldspar and in addition to having alumina and silica, has iron as one of its other constituents and this will give a colored clay. The quartz is but little decomposed by the different atmospheric agencies and remains as sand. The mica is only partially decomposed and flakes of mica are disseminated through the mass. The product of decomposition of such a granite would be a clay with more or less quartz, feldspar, mica and iron disseminated through it.

The feldspars, however, are not the only silicate minerals from which clay is formed. There is a very large number of these silicate minerals which, when they decompose, form some grade of clay and on account of the great variation in the composition of these, the final products of decomposition are very different. Not only do they differ in their chemical properties, but also in their physical properties. The character of the clay is in every case determined by the character of the rock from which it has been derived and since there are so many kinds of rocks, there must necessarily be great variation in the products,

due to their decomposition. White clays are exceptional, owing to the great abundance of iron-bearing minerals and when they do occur are usually more valuable than the colored clays, and are used in the manufacture of the better grades of clay wares.

Based on the position which they occupy as regards the rock or minerals from which they have been formed, clays may be separated into two classes, as follows: Residual clays, or those that remain in the place where they have been formed, and transported clays, or those that have been removed from the place where they formed and carried, for a greater or lesser distance, by some agency such as streams, glaciers, wind, etc., and then deposited. The clay deposits of Washington belong to both of these classes and both of them are important.

RESIDUAL CLAYS.

Where transportation has not kept pace with decay the material that remains forms a residual deposit, overlying the rock from which it was formed. The residual clays as a general thing are less complex in their mineralogical composition than the transported ones. The residual clays differ much from the transported ones in their physical conditions. In many cases these clays contain coarse fragments of any hard or very insoluble material which the original rock may have contained, such as quartz, fragments of chert, etc.

The extent and thickness of residual clay deposits will depend on a number of things, such as the extent of the rock mass from which they have formed, the climate, character of the rock, and topography of the locality.

TRANSPORTED CLAYS.

The transported clays are carried for longer or shorter distances and then deposited. Those clays that have simply been washed from the hillside to the valley below will have practically the same composition as the residual deposits from which they were derived. In this somewhat of a sorting process will have taken place and the coarser, heavier, materials will be separated from the clay. If the clay has been transported for long distances more or less foreign materials will occur with it. These

foreign substances are derived from various sources while the clay is being transported and are deposited with it.

The sedimentary clays of Washington have been separated by the writer into the following classes:

1. Estuarine clays.
2. Glacial clays.
3. Marine clays.
4. Lacustrine clays.
5. Flood Plain and terrace clays.

Estuarine Clays.

The estuarine clays are those that have been formed in shallow arms of the sea and on account of this they are apt to occur over long and comparatively narrow areas. Streams carrying sediments empty into these estuaries, and sediments are deposited and clay beds are formed. In case strong currents prevail in parts of the estuary the fine sediments will not be deposited at these places, but might be carried on through the estuary and out to sea, and form marine deposits.

Glacial Clays.

Glaciers exert more or less of a scouring action on the beds over which they flow, and this has a tendency to remove, not only the loose material which occurs on the surface, but also to grind up and remove more or less of the underlying solid rock materials which occur in the area traversed by the ice. This material may be transported for long distances and is redeposited by the melting of the ice. The material deposited by the melting of the ice will not be sorted, and will consist of various kinds of materials, as well as those which vary much in size from the very fine particles of kaolin to large gravels and boulders. Where these ice deposits have been modified by streams, the material has been more or less sorted and the deposits are more uniform both in composition and texture.

Marine Clays.

The marine clays include those sedimentary deposits which have been formed on the ocean bottom. They are laid down

where the water is practically free from currents and hence are usually formed some distance from the shore where the water is comparatively still. These deposits frequently cover large areas and are of great thickness.

Lacustrine Clays.

Lake clays are those that have been formed in basin-like depressions which were occupied by lakes or swamps. Streams carrying more or less sediment in suspension, have their velocity checked when they enter a lake and on account of this, deposit this material. The coarsest material will be dropped nearest the shore and the finest farthest from the shore. In this way the lake deposits are sorted, the sand and gravel occurring along the shore, while the particles of fine clay material are carried out into deeper water. These lake deposits, as a rule, are more uniform in composition and texture than some of the other classes of deposits and, as a result of this, some of the best clays belong to this class.

Flood Plain and Terrace Clays.

In the case of many streams terraces border them on one or both sides. There may be a number of these terraces, one above the other, and each one represents a former flood plain. These terraces, or benches, are often made up largely of more or less pure clays. On account, however, of the variation in velocity of the water from time to time, these deposits are often made up of alternate layers of clay, sand, and gravel. Clays of this class are quite common along many of the larger streams of Washington.

IMPURITIES IN CLAYS AND SHALES.

Clays.

Kaolinite, as it occurs in nature, is seldom absolutely pure, but has associated with it other minerals which may or may not make it suitable for the manufacture of Portland cement. If pure kaolinite were used, a certain amount of silica would be introduced, but the percentage of silica would be too small for the amount of alumina. The kind and amount of the minerals

found associated with kaolinite in clays will depend largely upon the materials from which the clay has been formed, and the conditions under which it has been deposited. The most common of the minerals, other than kaolinite, found in the clays are quartz, feldspar, mica, iron oxide, iron sulphide, calcite, gypsum and magnesia.

Quartz—Free silica or quartz in the form of small more or less rounded grains, is found in many of the different clays. The size of these particles varies much and ranges from those that are very small, a fraction of a millimeter, upward to almost any size. The amount is also very variable, and may be from a fractional part of one, to more than fifty per cent. In many places these materials have been finely ground by natural processes and before deposition took place, more or less of a sorting process has been carried on and the fine materials have been deposited in places and the coarser in others. The shales and the glacial clays represent deposits usually of these finer materials.

Mica—The term mica includes a group of minerals which vary somewhat in composition but which are all alike in that they are silicates of aluminum with other substances, as iron magnesia, calcium, and alkalies. Micaceous minerals are common constituents of the rocks from which clays are formed, resist weathering well, the shape of the particles as flakes causes them to float readily, and hence they occur in greater or lesser amounts in all clays. The combined silica in the mica will unite readily with the calcium at high temperatures and in this respect is the same as the feldspar.

The most common of the mica minerals is muscovite, K_2O $3 Al_2O_3$, $6 SiO_2$, $2 H_2O$, which in composition is very similar to orthoclase, the only difference being that it contains two more molecules of alumina and two of water.

Feldspar—The term feldspar, as used here, includes a group of minerals. These minerals vary in composition but are all of them, silicates of aluminum with either potash, soda, or

lime or mixtures of these. Orthoclase, or potash feldspar, is much the most common one of these minerals.

Feldspar is a very common constituent of the clays. The most of the igneous rocks from which the clays are formed contain feldspar and when these rocks decompose, particles of the feldspar are not completely decomposed and changed to clay. These particles are transported by water along with the clay and deposited with it. The particles of feldspar may be coarse or fine, depending on the amount of decomposition and grinding to which they have been subjected. Usually they are finer than the particles of quartz, as they are less resistant to mechanical abrasion, but coarser than the clay material.

The following table will show the difference in chemical composition of the type feldspars:

CHEMICAL FORMULA	PERCENTAGE COMPOSITION					Percentage Ratio of Silica to Alumina
	Silica (SiO ₂)	Alumina (Al ₂ O ₃)	Potash (K ₂ O)	Soda (Na ₂ O)	Lime (CaO)	
OrthoclaseK ₂ O, Al ₂ O ₃ , 6 SiO ₂	64.7	18.4	16.9	3.52 : 1
Albite Na ₂ O, Al ₂ O ₃ , 6 SiO ₂	68.7	19.5	11.8	3.52 : 1
AnorthiteCaO, Al ₂ O ₃ , 2 SiO ₂	43.2	36.7	20.1	1.18 : 1

The feldspars, like kaolinite, are double silicates. In the feldspars the second base as shown in the table above is one of the alkalis. On account of the silica being in the combined state it is readily available for cement making, as when heated in the kiln with lime it readily combines with it.

Shales.

Shales are simply hardened clays and hence have practically the same composition as clays and may contain any of the impurities discussed above as occurring in clays. Like the clays, they vary widely in chemical composition, but within a limited area they show as a general rule a much greater uniformity in texture and chemical composition. Shales are usually fine grained and have more or less well marked cleavage.

Shales, for various reasons, are used more to mix with limestone in the manufacture of Portland cement than clays. They

are often more favorably situated, with respect to the limestone, than are the clays. Shales are preferable to clays for mixing with limestone, since segregation of the two is less likely to take place. They also as a general thing carry less water and consequently do not require so much drying before grinding.

CHAPTER IV. HISTORY OF THE CEMENT INDUSTRY.

DEVELOPMENT IN EUROPE.

Who first discovered the binding properties of lime mortar and when is not known, but it is certain that its use antedates written history. On the Island of Cyprus are the remains of a very ancient temple that are thought to be the oldest ruins in the world and lime mortar is found between the stones here. In the building of the Pyramids, more than four thousand years ago, the Egyptians used a mortar in which partially burned gypsum or plaster of Paris was the cementing material. The Romans discovered that a mixture of lime and volcanic ashes would harden under water and they used this mortar in many of their public buildings, in the Pantheon, and in the aqueduct which supplied Rome with water. These volcanic ashes came mainly from Pozzuoli, at the foot of Vesuvius, and the mixture of this material with lime forms what is known as Pozzuolana cements, which are the oldest known hydraulic mortars. From the time of the Romans, however, to the latter part of the eighteenth century, practically no advance was made in hydraulic mortars and in spite of such ancient use of hydraulic cement, the industry is a comparatively recent one, the larger part of the development having taken place within the last fifty years.

The cement industry proper dates from the time when John Smeaton, an English engineer, was employed by parliament to build a light house upon a group of rocks, in the English channel, just off the coast of Cornwall. Two wooden structures, built upon these rocks, had been able to withstand the fury of the elements but a short time, and Smeaton determined to build a structure that would withstand the fiercest storms and be a lasting monument to his engineering skill. The mortars that were known and used at this time would not harden under water, and as the crags on which the lighthouse was to be built were under water for several hours during high tide, it was necessary,

in order that the foundations should be firm, that some mortar should be found that would harden in the presence of water.

With this object in view Mr. Smeaton, in 1756, undertook a series of investigations which finally lead to the discovery that the soft clayey limestones found at Aberthaw, in Cornwall, made a lime much superior to any then in use, not only because it hardened better in the air, but because it would also harden under water. The basis of the hydraulic mortar used in the construction of the Eddystone lighthouse was obtained from the burning of this limestone.

The first patent for cement manufacture was taken out by Joseph Parker, of Northfleet, in Kent county, England, in 1796. This was made by calcining, or burning the argillo-calcareous, kidney-shaped nodules, called "septaria," and afterward grinding the resulting product to a powder. These nodules in composition were very similar to what we now call Rosendale cement rock. He gave to this powder the misleading name of "Roman Cement," but it was practically what is now known as natural rock cement.

In 1802 the same kind of material was used in producing cement at Boulogne, France, and this was the beginning of the cement industry in that country. In 1810 Edgar Dobbs, of Southwick, England, obtained a patent for the manufacture of an artificial Roman cement by mixing carbonate of lime and clay in certain proportions. The mixture was then molded into bricks and heated sufficiently to drive off the carbon dioxide, but not to vitrify the mixture.

In 1818 St. Leger took out a French patent for making hydraulic lime. He calcined a mixture of chalk and clay, and the process is said to be continued by one of the French works, even at the present time. In 1822 James Frost took out an English patent for "a new cement or artificial stone," and in 1825 established works on the Thames and became the first manufacturer of artificial cement.

In 1824 Joseph Aspdin, a bricklayer of Leeds, England, took out a patent on an improved cement, which he proposed

to make by burning and grinding a mixture of limestone and clay, and called the product Portland cement, from the similarity in appearance of this artificial stone to a building stone much used in London, which was quarried on a bold headland extending out into the English Channel, known as the Portland Neck. Aspdin erected a factory at Wakefield, England, for the manufacture of his cement, which was used on the Thames tunnel in 1828. From 1828 to 1859, but little advance was made in the Portland cement industry. In 1859, however, John Grant, the engineer in charge of the construction of the London drainage canal, decided to use Portland cement as the material out of which to build it, and from that time on up to the present, the Portland cement industry has been gradually increasing until now it is a very important one.

The Portland cement industry in France began about 1850, in Germany in 1852, and in Belgium in 1872. In England, the growth of the Portland cement industry has been chiefly in the Thames and Medway districts, where the raw materials are the soft white and gray chalks and river mud. In Germany, the industry has developed in the northern and western parts, where the raw materials employed are chiefly soft chalks, marls, and clays. In southern Germany, Austria, and Switzerland, hard limestones are usually employed. In northern France chalks, marls, and clays are used.

DEVELOPMENT IN THE UNITED STATES.

The cement industry began in the United States with the discovery, in 1818, of a natural cement rock in Madison county, New York, along the line of the Erie canal, by Mr. Canvass White, an engineer in charge of construction work on the canal. A plant was erected at Chittenango, Madison county, N. Y., where a large part of the cement for the canal was made. In 1825, in the construction of the Delaware and Hudson canal, cement rock was discovered in Ulster county, N. Y., and very soon after this a mill was built at Rosendale, and this locality soon became the center of the industry. The cement made here

was called Rosendale, and this name is still largely applied to American natural cements.

During the early development of the cement industry in the United States, the largest amount of cement was being used in the construction of canals. These also furnished about the only means for the transportation of bulky materials and on account of these facts nearly all of the early mills were built along the line of some canal, to furnish cement for its construction. Thus natural cement rocks were found in western and central New York, in the Lehigh valley, in Pennsylvania, in the James, the Potomac, and Ohio river valleys and cements were made in all of these localities at comparatively early dates.

In 1829, while the Louisville and Portland canal was under construction, cement rock was discovered near Louisville, Ky., and the manufacture of cement was soon commenced there.

During the construction of other canals, cement rock was discovered in other places, as near Hancock, Md., Utica, N. Y., Balcony Falls, Va., and at Siegfried, Pa.

The manufacture of Portland cement began, experimentally, in the United States, at Coplay, Lehigh county, Pa., in 1872. The Coplay Cement Company had a plant here and had been manufacturing natural-rock cement for several years. Mr. David O. Saylor, who was president and superintendent of the company, carried on for several years investigations to determine the practicability of making Portland cement from the raw materials owned by the Coplay Cement Company. Many trial lots were burned and finally, in 1875, the company turned out its first real Portland cement. This cement showed over 300 pound test neat at seven days and in 1876 this company was awarded a medal for Portland cement at the Centennial Exhibition.*

According to Russell,† Portland cement was manufactured in Michigan about this same time.

*Mineral Industry, Vol. VI, p. 94.

†Twenty-second Annual Report, U. S. Geological Survey, Part III, p. 635.

"The history of the Portland cement industry in Michigan begins with the year 1872, when the Eagle Portland Cement Company, with headquarters at Chicago, built a cement plant about two miles northeast of Kalamazoo."

The materials used by this company were marl and clay and the plant was only in operation a few years.

From the building of the first plant in about 1872, until 1881 six different plants had been built in the United States, several of which, however, had been failures for one reason or another and had shut down, so that up to the beginning of the year 1881 only 124,000 barrels of Portland cement had been manufactured in the United States. From this time on, however, the production increased quite rapidly, until at the present time more than 100 plants are in operation and the production exceeds 75,000,000 barrels each year.

The following table shows the gradual growth of the Portland cement industry from its beginning to the close of 1911:

PRODUCTION OF PORTLAND CEMENT IN THE UNITED STATES, 1870-1911, IN BARRELS.*

Year.	Quantity.	Value.	Year.	Quantity.	Value.
1870-1879 ...	82,000	\$246,000	1896..	1,543,023	\$2,424,011
1880	42,000	126,000	1897..	2,677,775	4,315,891
1881	60,000	150,000	1898..	3,692,284	5,970,773
1882	85,000	191,250	1899..	5,652,266	8,074,371
1883	90,000	193,500	1900..	8,482,020	9,280,525
1884	100,000	210,000	1901..	12,711,225	12,532,360
1885	150,000	292,500	1902..	17,230,644	20,864,078
1886	150,000	292,500	1903..	22,342,973	27,713,319
1887	250,000	487,500	1904..	26,505,881	23,355,119
1888	250,000	487,500	1905..	35,246,812	33,245,867
1889	300,000	500,000	1906..	46,463,424	52,466,186
1890	335,500	704,050	1907..	48,785,390	53,992,551
1891	454,813	967,429	1908..	51,072,612	43,547,679
1892	547,440	1,153,600	1909..	64,991,431	52,858,354
1893	590,652	1,158,138	1910..	76,549,951	68,205,800
1894	798,757	1,383,473	1911..	78,528,637	66,248,817
1895	990,324	1,586,830	Total.	507,752,834	\$495,225,971

*Mineral Resources, U. S. Geological Survey, 1911, part II, p. 492.

The above table shows a very rapid growth of the Portland cement industry in the United States in the last fifteen years. By far the larger part of this cement is produced in the eastern states. Pennsylvania has been the leading state from the first, and had twenty-five producing plants in 1910, with a total pro-

duction of 26,675,978 barrels, or almost one-third of the total production of the United States for that year.

The price of Portland cement at the factory shows a gradual decline from \$3.00 a barrel in 1880, to 99 cents in 1901. From 1901 to the close of 1911, slight fluctuations occurred and for the year 1911 an average price of 84.4 cents per barrel for the whole country was obtained.

The following table gives the average factory prices of Portland cement per barrel in bulk from 1870 to 1911:

AVERAGE PRICE PER BARREL OF PORTLAND CEMENT, 1870-1911.*

1870-1880 ...	\$3.00	1893.....	\$1.91	1903.....	\$1.24
1881	2.50	1894.....	1.73	1904.....	.88
1882	2.01	1895.....	1.60	1905.....	.94
1883	2.15	1896.....	1.57	1906.....	1.13
1884	2.10	1897.....	1.61	1907.....	1.11
1885-1888 ...	1.95	1898.....	1.62	1908.....	.85
1889	1.67	1899.....	1.43	1909.....	.813
1890	2.09	1900.....	1.09	1910.....	.891
1891	2.13	1901.....	.99	1911.....	.844
1892	2.11	1902.....	1.21		

*Mineral Resources, U. S. Geological Survey, 1911, part II, p. 492.

The production of natural cement in the United States from its first manufacture in 1818 until 1899, when the maximum production was reached, is shown in the following table. The industry was most prosperous during the period from 1887 to 1903. Beginning with 1904 it has shown a continuous decline in production each year and the production for 1911 is the lowest on record for over thirty years.

PRODUCTION OF NATURAL CEMENT IN THE UNITED STATES, 1818-1911, IN BARRELS.*

Year.	Quantity.	Year.	Quantity.	Year.	Quantity.
1818-1829 ...	300,000	1887..	6,692,744	1900..	8,383,519
1830-1839 ...	1,000,000	1888..	6,253,295	1901..	7,084,823
1840-1849 ...	4,250,000	1889..	6,531,876	1902..	8,044,305
1850-1859 ...	11,000,000	1890..	7,082,204	1903..	7,030,271
1860-1869 ...	16,420,000	1891..	7,451,535	1904..	4,866,331
1870-1879 ...	22,000,000	1892..	8,211,181	1905..	4,473,049
1880	2,030,000	1893..	7,411,815	1906..	4,055,797
1881	2,440,000	1894..	7,563,488	1907..	2,887,700
1882	3,165,000	1895..	7,741,077	1908..	1,686,862
1883	4,190,000	1896..	7,970,450	1909..	1,537,638
1884	4,000,000	1897..	8,311,688	1910..	1,139,239
1885	4,100,000	1898..	8,418,924	1911..	926,291
1886	4,186,152	1899..	9,868,179	Total.	230,705,233

*Mineral Resources, U. S. Geological Survey, 1911, part II, p. 512.

The contrast between the growth of the Portland cement industry and the decrease in the production of natural cement in the last ten years is very significant of the efficiency and popularity of Portland as compared with natural cement.

DEVELOPMENT IN WASHINGTON.

In Washington the first development work was done on the deposit a little above Box Canyon on the Pend O'Reille river. This deposit was discovered and located in January, 1901, by Mr. F. G. Jordan. Considerable work was done in developing power by bringing water from Cedar creek along the side hill to the place where the plant for the manufacture of natural hydraulic cement was to be located. The town of Cement was located and a postoffice established. A small plant was built, and in February, 1904, the first natural hydraulic cement was manufactured in Washington. The output of the plant, however, never amounted to anything, contests were started over the deposits, and nothing more has been done here in the way of cement manufacture. It was the idea of the original promoters to establish a Portland cement plant at this place, but this has never been done.

The first Portland cement made in Washington was by the Washington Portland Cement Company, at Concrete, on the Skagit river, in Skagit county. Work was started on this plant June 1, 1905, and the first cement was made in May, 1907. The plant to start with had two kilns, each $7\frac{1}{2}$ feet in diameter and 100 feet long, and a capacity of 900 barrels per day. In the spring of 1911, two additional kilns, each 8 feet in diameter and 125 feet long were installed. This increased the capacity 1,700 barrels a day, making the total capacity of the plant 2,500 barrels per day.

The next cement plant to be built in Washington was the Superior Portland Cement plant, located at Concrete, just across the Baker river to the west of the Washington plant. This was built soon after the Washington plant, and for a number of years these were the only Portland cement plants in operation in Washington.

In June, 1910, work was started on the plant of the Inland Portland Cement Company, at Metaline Falls, and April 1, 1911, it was completed. The construction of a plant at this point involved also the development of a large water power and this was not completed until August, so that the plant was not in operation until this time.

The plant of the International Portland Cement Company, which is located in Irvin, nine miles east of Spokane, was begun in January, 1912, and the first cement manufactured one year later.

The Olympic Portland Cement Company, Limited, at Bellingham, was the first plant in Washington to use the wet process in the manufacture of Portland cement. The work of building this plant was begun in the fall of 1911, and it has been in operation for some time now.

In the fall of 1912 work was begun on the plant of the Idaho Portland Cement Works, at Asotin, Washington, and it should not be long now before this plant will be manufacturing cement.

From the above it is seen that the development of the Portland cement industry in Washington has been quite rapid, the first plant actually beginning operations in 1907, while at the present time (July, 1913) five plants are in actual operation, and a sixth one almost done.

PORTLAND CEMENT.

USE OF THE TERM PORTLAND.

The name Portland cement was first given to an artificial compound of lime and clay prepared by Mr. Joseph Aspdin, a Leeds bricklayer. This name was chosen by him on account of the fancied resemblance in color and texture of his hardened cement to the oolitic limestone that occurred on the Island of Portland and was highly regarded in England as a building stone.

The specifications used by Aspdin, and dated October 21, 1824, are as follows:*

“I take a specific quantity of limestone, such as that generally used for making or repairing roads, after it is reduced to a puddle or powder; but if I can not procure a sufficient quantity of the above from the roads, I obtain the limestone itself and I cause the puddle or powder, or the limestone, as the case may be, to be calcined. I then take a specific quantity of argillaceous earth or clay, and mix them with water to a state approaching impalpability, either by manual labor or by machinery. After this proceeding I put the above mixture into a slip pan for evaporation, either by the heat of the sun or by submitting it to the action of fire or steam conveyed in flues or pipes under or near the pan, until the water is entirely evaporated. Then I break the said mixture into suitable lumps, and calcine them in a furnace similar to a lime kiln till the carbonic acid is entirely expelled. The mixture so calcined is to be ground, beat, or rolled to a fine powder, and is then in a fit state for making cement or artificial stone. This powder is to be mixed with a sufficient quantity of water to bring it into consistency of mortar and thus applied to the purposes wanted.”

At present there is quite a general agreement of opinion as to what is understood by the term Portland cement. There are, however, a few points about which there is still differences of opinion. On account of this the definitions of the term given in specifications are often vague and unsatisfactory.

There is a general agreement as regards the fact that the cement mixture must consist essentially of lime, silica, and alumina in proportions which can vary but little and that this mixture must be burned at a temperature high enough so that a partially fused mass known as “clinker” will be formed. The above points must each of them therefore be included in any complete definition. The point in regard to which there is the most difference of opinion is as to whether or not cements made from a natural cement rock by burning it should be considered true Portlands.

*Calcareous Cements, their nature, manufacture, and uses. Redgrave and Sprachman, p. 31.

In France and Belgium especially the products derived from burning natural rock, without artificial mixture, at comparatively low temperatures are considered as Portland cements. While these may not be especially high grade Portland cements, at the same time there appears to be but little ground for excluding them from this class of materials.

Theoretically, a rock could occur which would have lime, silica, and alumina in such proportions that when burned it would give a good Portland cement. It is very seldom, however, that this actually happens and where the natural cement rock is used the composition is corrected by the addition of other materials to it before it is burned.

The following definition is the one used in specifications prepared by the Corps of Engineers of the U. S. A. :* —

“By a Portland cement is meant the product obtained by 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.”

Mead† says Portland cement may be defined as “The finely pulverized product resulting from the calcination to incipient fusion of an intimate mixture of properly proportioned argillaceous and calcareous materials and to which no addition greater than three per cent. has been made subsequent to calcination.”

The above definitions do not require pulverizing or artificial mixing of the materials before burning and hence would admit the “natural Portlands” of Belgium and France.

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

†Portland Cement, p. 15.

Eckel objects somewhat to this definition of Portland cement, especially when applied to American Portland, and proposes this definition:*

“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).”

According to the above definition, Portland cements can be made only from artificial mixtures of lime, silica, and alumina that are finely pulverized before burning.

The above definitions indicate the main differences as regards the present use of the term Portland cement.

COMPOSITION AND CONSTITUTION.

There has been much discussion in the past by many investigators as to what Portland cement really is. This question has been attacked in various ways, such as mineralogical examinations, chemical analysis, study of synthetic mixtures, study of heat reactions, etc. An ordinary chemical analysis of a specimen of cement will determine the elements that are present in the cement and in what proportions they exist. By a comparison of a large number of such analyses some conclusions may be drawn as to the probable limits of composition of good Portland cement. These analyses, however, fail completely to give any information in regard to the constitution of Portland cement. They give no information in regard to the manner in which these elements are united, mineralogical composition. They fail to show why some cements are good while others are poor; and they afford no explanation of the setting properties which the powdered clinker possesses. The closest approach to an accurate conception of the structure of Portland cement appears, however, to have been made by the microscopic study to determine the mineralogical composition.

*Iowa Geological Survey, Vol. XV, p. 53.

The first work along this line was done in 1887. By this method of study, LeChatelier and another investigator by the name of Tornebohm, working independently of each other, identified in Portland cement clinker four distinct mineral constituents which were described by Tornebohm* and named Alit, Belit, Celit, and Felit.

"Alit is the preponderating element and consists of colorless crystals of rather strong refractive power, but of weak double refraction. By this he means the alit in polarized light between crossed nicol prisms has insufficient optical activity to produce more than weak bluish gray interference colors."

"Celit is recognized by its deep color, brownish orange. It fills the interstices between the other constituents, being the magna or liquid of lowest freezing point out of which the alit is separated. It is strongly double refractive, that is to say, gives brilliant colors when examined between crossed nicol prisms."

"Belit is recognized by its dirty green and somewhat muddy color, and by its brilliant interference colors. It is biaxial and of high index of refraction. It forms small round grains of no recognized crystalline character."

"Felit is colorless. Its index of refraction is nearly the same as that of belit and it is strongly double refractive. It occurs in the form of rounded grains, often in elongated form, but without crystalline outline. Felit may be entirely wanting."

"Besides these minerals an amorphous isotropic mass was detected by Tornebohm and Le Chatelier. It has a very high refractive index.

"Tornebohm adds the important fact that a cement four per cent. richer in lime than usual consists almost entirely of alit and celit."

In a paper read before the Association of Portland Cement Manufacturers, at Atlantic City, N. J., June 15, 1904, Dr. Clifford Richardson described the results of a very thorough exhaustive microscopic study of Portland cement clinker. As a result of this study he arrives at the conclusion that pure clinker consists of two distinct solid solutions, alit and celit,

*Eckel, Cements, Limes, and Plasters, pp. 568-569.

the first being tri-calcic aluminate dissolved in tri-calcic silicate, the second di-calcic aluminate dissolved in di-calcic silicate. These, though invisible in the molten state, are not so in the solid state. The limits of the proportions of alit and celit depend on the basicity and the ratio of silicate to aluminate and are roughly 3 to 1 and 6 to 1. This theory of solid solution was, however, by no means a new one, as it was first advanced about 1858. Richardson prepared many synthetic silicates and aluminates and determined their optical properties, hydraulic value, and physical characteristics. The investigations, the results of which are given in this paper, are the most thorough so far undertaken and the paper is the most valuable argument that has been advanced to explain the properties of Portland cement along the lines of physical chemistry.

“In 1906 Day and Shephard stated that they had found by microscopic tests that no such compound as tri-calcium silicate existed and that what Newberry, Le Chatelier, and Richardson had supposed to be this compound, was nothing more than a solution of lime in calcium orth-silicate or di-calcium silicate (2 CaO SiO_2). Their statements were so amply backed by proof that it is now generally agreed that Portland cement is probably nothing more than a solid solution of lime in a magma of orth-silicates and orth-aluminates of lime. It is, therefore, as impossible to assign to Portland cement any definite chemical symbol as it is to assign one to steel, which is a solid solution of carbon, etc., in iron, or to alloys, which are also solid solutions. At the same time the composition of Portland cement has a great bearing upon its physical properties, just as does the composition of an alloy on its physical properties.”*

The following table gives the results of analyses of Portland cements made in different parts of the United States and from various materials.†

*Maryland Geological Survey, Vol. 8, pp. 277-278.

†Meade, R. K., Portland Cement, p. 29.

ANALYSES OF AMERICAN PORTLAND CEMENTS.

Made From	Where Made	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	Loss
Cement-rock and limestone	Nazareth, Pa.	19.92	2.28	7.52	62.48	3.19	0.52	0.66	1.51	1.46
	Nazareth, Pa.	21.14	2.30	6.94	63.24	3.26	0.36	0.51	1.12	1.24
	Bath, Pa.	19.64	2.80	7.52	62.31	3.04	n. d.		1.60	1.48
	Alpha, N. J.	21.82	2.51	8.08	62.19	2.71	n. d.		1.02	1.05
	Northampton, Pa.	21.94	2.37	6.87	60.25	2.78	0.61	0.87	1.88	3.55
	Coplay, Pa.	22.26	2.10	5.36	63.32	3.81	n. d.		0.89	1.24
	Omrod, Pa.	22.20	2.27	6.69	62.61	3.00	0.32	0.61	1.32	1.56
	Martin's Creek, Pa.	20.32	2.50	7.12	62.94	3.38	n. d.		1.45	1.25
	Reading, Pa.	24.16	1.45	5.10	62.95	3.12	0.21	0.50	1.35	1.40
Limestone and clay or shale	Bay City, Mich.	20.72	2.85	7.17	62.64	1.97	0.48	0.12	1.42	2.58
	Wellston, O.	21.84	5.05	6.77	62.66	0.80	n. d.		1.24
	Chanute, Kan.	20.74	3.72	7.06	62.76	1.78	0.41	0.23	1.12	1.40
	Ada, Okla.	12.28	3.20	6.36	59.66	3.11	0.80	0.25	1.40	2.82
	Stroh, Ind.	21.78	2.65	7.31	62.35	2.88		0.47	1.78	0.78
	Glens Falls, N. Y.	21.50	10.50	63.50	1.80		0.40		1.50	n. d.
	Alsen, N. Y.	23.94	3.20	5.62	62.32	1.77	n. d.		0.90	1.68
	Fordwick, Va.	21.31	2.81	6.54	63.01	1.71	n. d.		1.42	2.01
	Davenport, Cal.	25.38	1.20	3.34	62.96	2.20	n. d.		0.35	4.58
	Cement, Cal.	22.34	3.30	7.00	60.72	1.90	n. d.		1.05	2.54
Baker, Wash.	24.63	8.56	62.88	1.60		n. d.		1.33	n. d.	
St. Louis, Mo.	23.12	2.49	6.18	63.47	0.88	n. d.		1.34	1.81	
Demopolis, Ala.	19.36	4.10	9.18	63.20	1.16	n. d.		1.18	1.12	
Marl and clay	Portland, Col.	21.88	2.85	7.14	64.94	Tr.	1.18		0.73	1.08
	Middlebranch, O.	21.24	4.14	7.85	63.22	0.28	0.68		1.11	1.32
	Coldwater, Mich.	21.22	3.83	7.51	63.75	0.82	n. d.		1.53	1.02
	Sandusky, O.	21.93	2.35	5.99	62.92	1.10	0.63	0.27	1.55	2.92
	Bronson, Mich.	22.90	3.60	6.80	63.90	0.70	1.10		0.40	0.60
	Harper, O.	21.30	2.00	6.95	62.50	1.20	n. d.		0.98	4.62
Warners, N. Y.	22.04	3.41	6.45	60.92	3.53	n. d.		1.25	
Limestone and blast furnace slag	Chicago, Ill.	22.41	2.51	8.12	62.01	1.68	n. d.		1.40	1.02
		23.06	2.88	8.16	62.10	1.88	0.36	0.58	1.57

The following table shows the limits in composition* within which most Portland cements of good quality will come:

COMPOSITION OF PORTLAND CEMENT.

	Maximum.	Minimum.	Average.
Silica (SiO ₂)	20%	24%	22%
Alumina (Al ₂ O ₃)	5	9	7.5
Iron oxide (Fe ₂ O ₃)	2	4	2.5
Lime (CaO)	60	63.5	62.0
Magnesia (MgO)	1	4	2.5
Sulphur trioxide	1	1.75	1.5

The above table shows a low range in composition for Portland cement, and proves the very great importance of careful proportioning the raw materials in its manufacture.

*Meade, R. K., 7th Congress of Applied Chemistry; see Chemical Engineer, Vol. X, p. 184.

CHAPTER V.

EXAMINATION OF CEMENT MATERIALS AND LOCATION OF PLANT.

The determining of the possible value of any deposit of raw material for the manufacture of Portland cement is a complex problem, depending upon a number of different factors. Some of the most important of these are: (1) chemical composition of the material; (2) physical character of the material; (3) amount of material available; (4) location of the material with reference to transportation facilities; (5) location of the deposits with reference to fuel supplies; (6) location of the deposits with reference to market.

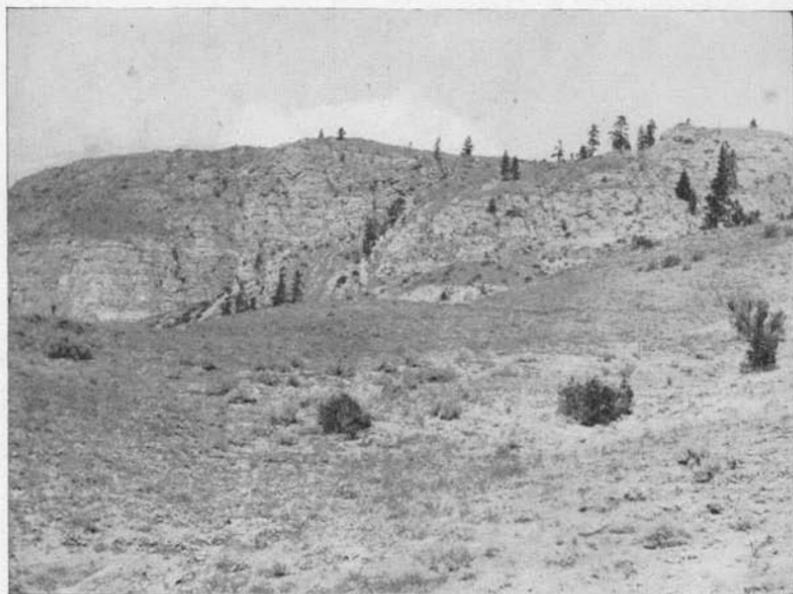
CHEMICAL COMPOSITION.

The percentage of the different elements in Portland cement varies more or less, but at the same time the composition of the raw materials must come within certain limits. The deposits should be carefully prospected, thoroughly sampled, and thorough analyses made of the samples. The analyses of the limestone should show as small a percentage as possible of magnesia carbonate, the maximum that it allowable being about 5 per cent. The limestone must be practically free from silica in the form of sand, chert, or flint. If the stone is a natural cement rock or a clayey limestone there should be a certain ratio between the alumina plus the iron and the silica. That is, the amount of silica should not be less than two nor more than three and one-half times that of the alumina and iron together. Sulphates should be present only in very small amounts.

Clays or shales should be free from sand, gravel, and materials of this character. They should be low in magnesia, alkalis, sulphides, and sulphates. The ratio between the silica, alumina, and iron should be the same as given above for the limestones.



A. Lime Hill, on Snake River, Asotin County.



B. Limestone Deposit near Riverside, Okanogan County.

PHYSICAL CHARACTER OF MATERIALS.

The physical character has much to do in determining the value of limestone, clay, or shale deposits for Portland cement. The harder the material, other things being equal, the more expensive it will be to quarry and grind it. The more moisture the material contains, the more heat it will take to dry it and this often adds very materially to the cost of manufacture.

AMOUNT OF MATERIAL AVAILABLE.

The construction of a Portland cement plant requires a very large investment and hence the amount of available material should be sufficient to last for not less than twenty-five years. In determining the available quantity of material, the first step is to measure the thickness, not along the surface of outcrop, but along a line perpendicular to the planes of stratification. With the thickness determined, it is usually an easy matter to determine the extent and then to calculate the quantity of material. If, for instance, a limestone deposit 100 feet thick outcrops and can be followed for a distance of 2,000 feet and can be worked to a depth of 100 feet along the dip, the number of cubic feet that could be quarried would be $100 \times 2000 \times 100$. This product multiplied by 160, which is approximately the weight of a cubic foot of limestone, and divided by 2,000 would give the value in tons which in this case would amount to 1,600,000 tons. A cement plant will use an average of about 15,000 tons of dry limestone per kiln each year. At this rate the above quantity of limestone would last a four-kiln Portland cement plant for over 40 years. If shale were mixed with the limestone about 5,000 tons per kiln, or 20,000 tons for a four-kiln plant, would be required each year. If the shale is to last for as long a period as the limestone, there should be a little more than 800,000 tons available. The quantity of shale, as to tonnage, is calculated in the same way the limestone was, except that the shale is estimated as weighing about 125 pounds per cubic foot.

LOCATION OF MATERIAL WITH REFERENCE TO TRANSPORTATION FACILITIES.

For its value, Portland cement is a heavy, bulky material, and hence the value of a deposit of Portland cement material is

much influenced by its location as regards transportation routes and markets. Unless the deposits are near a railroad or water route along which the raw materials and the finished product may be moved economically, the deposits are very apt to be of little or no value, as the cement made from these deposits cannot compete with that made from deposits more favorably situated. To secure satisfactory freight rates the deposits should be near friendly transportation lines or where low rates may be secured through the competition of several carriers. The deposits should be as near as possible to large and well established markets so that the margin between the cost of manufacture and the selling price may not be absorbed by freight charges.

LOCATION OF THE DEPOSITS WITH REFERENCE TO FUEL SUPPLY.

The location of cement deposits with reference to fuel is also an important item. Where coal is used in the plant as the fuel for burning the cement and as the source of power for driving the machinery from 200 to 300 pounds have been consumed for every barrel of Portland cement manufactured. In some places oil is being used in place of coal for burning the cement and in the western states especially where water-power is so plentiful, electricity is used as power to drive the machinery. The fuel consumption is one of the largest items in the cost of manufacture of Portland cement and naturally the more favorably the deposits are situated as regards fuel, other things being equal, the more valuable they will be.

The coals vary much as regards their value for use in the kilns in the burning of Portland cement. Those that are well suited for this purpose are the bituminous coals that are high in volatile matter and correspondingly low in fixed carbon. The high carbon coals will give higher temperatures than the bituminous coals, but on account of the slower combustion when pulverized and blown into the klin, the results are less satisfactory. The coal should have not more than two or three per cent. of sulphur and if entirely free from it, so much the better. The amount of ash in the coal should be low for at least

two reasons. First, because a large amount of ash decreases the heating value of any given volume of coal and second, because a considerable part of the ash goes into the mixture and if this were in large amounts it might have a detrimental effect on the finished product.

LOCATION OF THE DEPOSITS WITH REFERENCE TO MARKETS.

A deposit of cement material might satisfy all of the requirements discussed above, and still have little or no value on account of a poor market for the finished product. The deposits should be so situated that a local market area may be developed, within which cement produced by a plant in this locality may sell on a practically non-competitive basis. This local market should be great enough to take the larger part of any plant built to utilize the deposits. In addition to the local market area the deposits should be so situated that the manufactured cement may have easy access to a larger though competitive market area.

EXAMINATION OF DEPOSITS OF CEMENT MATERIAL.

As has been stated in the preceding pages, the chemical composition of the materials to be used in the manufacture of Portland cement must be very carefully determined in order to know whether the chemical constituents are present in the proper proportions or whether these proportions can be produced by certain mixtures of the materials. In order to know this, a thorough prospecting and sampling of the deposits must be made and the samples very carefully analyzed. The whole success of the undertaking depends upon the care, manner, and accuracy with which this sampling is done.

Different methods of examination may be used, but one of the most important things to be kept in mind is that no matter what the method, the results are of no value unless the samples analyzed represent truly the character of the deposits. The majority of the limestone, clay, or shale deposits vary more or less in composition, not only as regards the different layers of

which they are composed, but in different parts also of the same layer.

LIMESTONE.

In the case of limestones, where they are exposed in high bluffs, or where the strata are inclined and come to the surface, the individual layers may be examined to a considerable depth. In other cases drilling will be a very satisfactory method of prospecting the deposit. In fact, some persons contend that drilling is the only satisfactory way of prospecting limestone deposits. The method, however, to be used in many cases at least, will depend very largely on local conditions and in some cases it would seem that drilling is unnecessary.

Where the deposits lie flat and there are no streams that have cut deep gorges across the beds, so as to expose the different layers, then about all one can do to obtain samples from below the surface is to drill down into the beds. If the beds are inclined, however, and are exposed on the surface, then the different layers may be examined directly. The samples, in any case, should be taken so that all the rock to be used will be represented in the sample. They should be taken in the same position as regards each bed, that is, if one bed is sampled perpendicular to the bedding planes, the others should be also.

The surface rock is nearly always affected more or less by atmospheric agencies, and on account of this, samples of the fresh, unweathered material should be obtained, and in order to do this drilling will be resorted to in many cases. Various kinds of drills are in use for this purpose and each individual will have to determine largely for himself what particular kind he will use. Before the drilling is begun, the surface dirt should be cleared away and the surface rock exposed. The holes should be protected so that no surface material can get into them and contaminate the samples. If the deposit is to be thoroughly prospected a topographic map should be made of it and this may then be divided into squares, the length of the square being determined by the amount of drilling thought necessary to determine the character of the deposits. With such a map, drill-

ing can be carried on systematically, holes being put down at the points where the lines intersect or at the corners of each square and the material brought up by the drill saved for analysis. In some cases a single composite sample is taken from each hole, and in others samples are so taken that they represent each successive five, ten, or fifteen feet, as it may be, of the deposits passed through. In any case, however, the sample should be so taken that every inch of rock through which the drill passes will be represented.

Diamond drills are much used in prospecting cement materials and have some advantages over the ordinary churn drill. They cut a round cylinder of rock from one to two inches in diameter which may be brought to the surface and examined. These cores will show the texture and hardness of the material. They will show whether the beds are stratified or not and whether they have any thin layers of foreign substances, as quartz or clay. These drills are especially valuable when the beds are inclined and it is desired to drill holes perpendicular to the bedding planes. The one main objection to this class of drills is that they are expensive.

CLAY.

In looking for a clay that may be used in the manufacture of Portland cement, the experienced prospector takes advantage of all natural and artificial excavations wherever they expose the country rock in the locality under investigation. He follows up the rivers and studies the formations on either side, he examines the exposures in railroad cuts and in the quarries. He examines the various clay outcrops and where they appear favorable, takes preliminary samples and has them analyzed.

If any of the preliminary samples show satisfactory composition and physical properties, an opening should be made into the deposit and samples taken from within the bank. After a certain amount of preliminary work has been done it will be possible to determine whether it is worth while to make a thorough examination of the deposit or not.

If a thorough examination is decided upon it should be carried out in a systematic manner and along the same general

plan as that outlined above for the examination of limestones. The survey and examination should include a tract of land amply large enough to supply material sufficient for the capacity of the plant that it is the intention to build.

After the land has been mapped topographically, the map should be divided up into squares, the length of the sides of the squares being determined partly by the thickness and apparent uniformity in composition of the deposits. The same precautions should be taken in reference to the clay samples to see that they are representative, as with the limestone samples.

The clay samples may be obtained in various ways, such as digging down through the bed to be examined, boring with an auger, drilling with churn drill, churn drill and auger combination method, or core drilling. In the digging of pits the samples, of course, are large and are the most representative. The pits also give a chance for the direct observation of the deposits as deep down as they are dug. Ultimately, a few of these test pits should be dug, but as they are somewhat expensive, they should not be dug until a considerable amount of prospecting has been done in other ways and the indications are very good that the deposits will prove satisfactory.

The auger is probably the most successful implement with which to prospect most clay deposits and should be used much more extensively than it is. A two-inch auger is the most convenient, where only small samples are required. This may be operated by one man, and a depth of from twenty-five to thirty feet easily obtained. If larger samples are desired a larger auger may be used, but the work becomes more difficult, and hence much slower. The augers are most conveniently operated when so arranged as to use gas pipe, screwing on additional joints from time to time as depth is obtained and they are needed.

The common churn drill, such as is universally used in hard rocks, may also be used and if the deposits are hard it is very effective. In some cases a pipe which has sharp teeth at the end, is used and is forced down into the soft clay by twisting a long handle. In this case the sample will be a cylinder of the

clay filling the pipe, representing a thickness of clay equivalent to the length of clay cylinder. Another method is to sharpen the edges of one end of a pipe and then to drive this into the clay. In each of these methods the sample of clay is removed from the pipe, and additional sections added to the pipe as they are needed on account of depth reached.

SHALE.

In some cases shales are hard, while in others they are soft like clays. If they are hard, they will be treated much as the limestones are and some of the methods given for sampling them, may be used satisfactorily on the shales. If they are soft, however, then the methods applied to the clays will be found more satisfactory.

LOCATION OF THE FACTORY.

The location of the factory as regards the raw materials is a very important economic factor in the manufacture of Portland cement and one that should be given very careful consideration. From an economic point of view an ideal location is one in which the location of the shale and limestone is such that the factory may be placed in such a position that these may be conveyed to it by gravity. In some cases limestones and shales are found in such a position that the quarrying of one will uncover the other and where this is the case, it will reduce the expense somewhat of getting the raw materials, as it will obviate the necessity of additional stripping.

When shales and limestones are used in the manufacture of Portland cement, about 75 per cent. of the material used is limestone, which is composed essentially of calcite or calcium carbonate, and about 25 per cent. is argillaceous materials. Should the limestone contain a considerable amount of clayey material it might be necessary to add a purer limestone. On the other hand, if the limestone is very pure there must be an increase in the percentage of those materials consisting essentially of silica, alumina, and iron. This increase may be brought about by the addition of shale, clay or argillaceous limestone. Thus it is seen that limestone is much the largest ingredient of

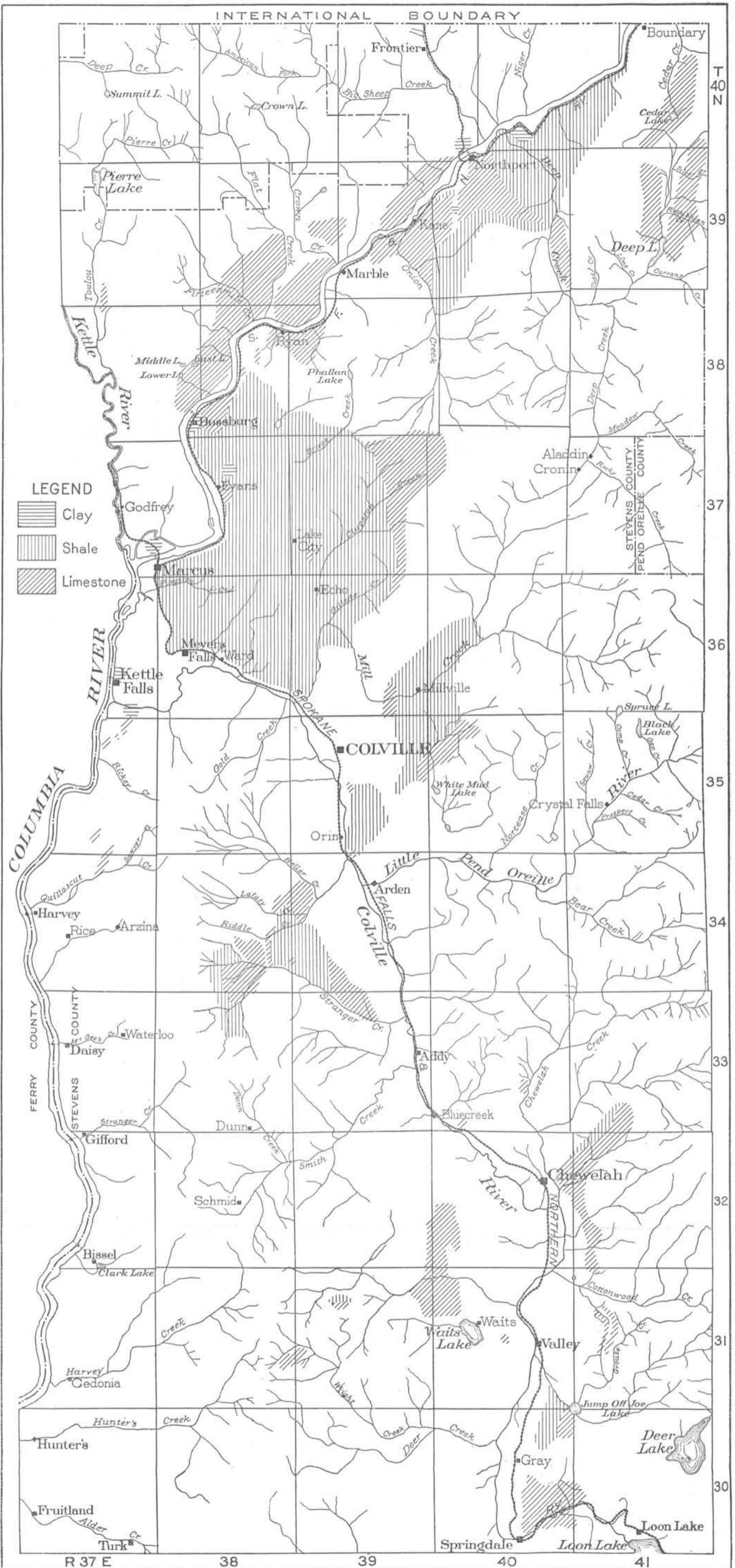
the cement mixture. Hence, in choosing a location for a cement plant which uses three times as much limestone as shale, the location with reference to the limestone is much more important than with reference to the shale.

The factory should be, for several reasons, located as near the raw materials as possible. Deposits of limestone, clay, or shale are not absolutely constant in composition and, on account of this fact, a constant check has to be kept on the materials by means of chemical analyses. In the same way a constant check must be kept on the finished product. If the plant is a considerable distance from the deposits of raw material it would probably be necessary to equip and maintain a chemical laboratory at the quarry and another at the factory, and this would mean extra expense.

In case the factory is not situated near the deposits, a much larger storage capacity for raw materials would be necessary. This would be due partly to the fact that the deposits are not absolutely constant in composition and the different grades must be kept separate so as to be able to tell the amount of each ingredient, as limestone, clay or shale, that should be used in order to give the finished cement the proper composition. Then, again, there should always be sufficient raw material on hand so that if anything should happen to prevent the delivery of the raw materials to the factory for a few days, it would not have to be closed down.

When the factory is located at a distance from the raw materials there will be the added cost of transportation and more handling. The raw materials lose a considerable amount in weight when burned. This loss is largely carbon dioxide and moisture. In the case of some clays and shales there is an additional loss due to organic matter.

“In the case of hard and comparatively dry limestones or shales, it may be considered that the raw material loses 33 1-3 per cent. in weight on burning. Converting this relation into pounds of raw material and clinker, we find that 600 pounds of dry raw material will make about 400 pounds of clinker. Allowing something for other losses in the process of manufacture, it



Map of a part of Stevens county, showing the location of deposits of Clay, Shale and Limestone.

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 limestone, 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 700 pounds of such a mixture would be required to make one barrel of finished cement.”*

*Iowa Geological Survey, Vol. XVII, p. 53.

CHAPTER VI.

MANUFACTURE OF PORTLAND CEMENT.

The process of manufacture of Portland cement may be grouped into two general classes, commonly called the dry and the wet process. The former is the one in most general use in this country, the latter being used mainly at those plants situated in the northern states where the lime content of the materials used is obtained from fresh water marls.

The manufacture of Portland cement by the dry process is naturally divisible into a number of distinct parts, the following being the most important:

1. Mining, haulage, and preparation of the raw materials.
2. Proportioning of the raw mixture.
3. Burning of the raw mixture.
4. Grinding of the clinker.

The methods to be used in mining the raw materials will vary much, depending largely upon the character of the material and the conditions under which it exists.

MINING OF LIME MATERIALS.

In the mining of calcareous materials, depending on their character, any of the following methods may be used:

Quarrying, dredging, steam shovel work, mining.

QUARRYING.

This method is used only in the working of limestone or cement rock deposits. In most cases the deposit is opened up on a low hillside so as to give a long working face with a small amount of stripping. The rock is usually blasted down in one or more benches, depending on the height of the face exposed. Power drills should be employed and these may be operated by steam, compressed air, or electricity. After the rock is broken down by blasting, the larger pieces are either reblasted or broken by sledging until they are reduced to such a size that they may be easily handled. The material is then loaded into carts or small cars and taken to the preliminary crusher.

In case the quarry contains several beds of rock which differ in composition and which lie horizontal, it may be worked in benches and tracks run in on each bench and in this way the different grades of material may be kept separate.

DREDGING.

This method is applicable only in the case of calcareous marls, such as are found in Michigan and Indiana. In most cases these marl deposits are covered with water and in this case the excavator is mounted on a barge. Marls contain a large amount of water and this has to be handled, and the weight of the marl needed to make a barrel of cement would be much greater than that of hard limestone.

STEAM SHOVEL WORK.

In some few cases the steam shovel is used to load the rock into the cars after it has been broken down by blasting. In the case of soft calcareous materials, such as chalk, dry marl, and soft limestones, the steam shovel may be used very successfully and the deposits worked very economically.

MINING.

This term as used here has reference to methods of obtaining any kind of raw materials by underground workings, through shafts or tunnels. Mining methods are seldom used in winning Portland cement materials. This is due very largely to the low value per ton of these materials and the fact that quarrying is an expensive method of winning them. In some few cases, however, conditions are such that this method may be used. If mining methods are to be employed there should be a thick layer of hard strong material above the deposit to be quarried. In this case less timber would be required and reduce somewhat the amount of dead work to be done and hence would cheapen the cost of mining the material.

WINNING OF CLAYS.

The winning of clays may be accomplished by the following methods, the one to be used in each case depending largely upon the nature of the clay:

Hand digging, quarrying, use of plow and scraper, steam shovel, dredging, and mining.

HAND DIGGING.

This method is in use mainly where the amount of clay used is small and where it is soft enough so that it can be dug with pick and shovel without too much effort. Clay deposits are often worked in benches on account of the fact that some parts of the deposit are of such a composition that they cannot be used and hence, must not be mixed with the good clay. The more of this poor clay that has to be moved, the more expensive the good clay.

QUARRYING.

This method is often used where the clay is too hard to be dug with pick and shovel or where large amounts are being used. The material is usually broken down by blasting, black powder being used in most cases. The clay is then broken up and may be loaded onto cars by hand or by steam shovel. The deposits are usually worked in benches much the same as limestone quarries.

PLOW AND SCRAPER.

In the case of large areas of soft clays, the plow and scraper may be used very satisfactorily. In case the material is to be moved only a short distance, the common scraper may be used, but for distances of from 200 to 500 or 600 feet wheel scrapers may be employed. In case of greater distances a platform may be used onto which the scrapers may be drawn and the clay dumped through a grating into a cart, wagon, or car below.

STEAM SHOVEL.

The steam shovel may be used very profitably in the winning of some clays. These are made in various sizes and are capable of handling from 400 to 5,000 cubic yards per ten hours. For the handling of clay for a cement plant, the smaller sizes would be all that would be necessary. Where the steam shovel is used the cost of winning clay is less than by any other method.

DREDGING.

This method may be practiced in procuring clay from river or lake bottoms, or in very low wet places. It is but little used, however, and needs no general descriptions.

MINING.

This method of winning clay is used only when absolutely necessary. It is a very expensive method under even the most favorable circumstances. The cost of mining will depend largely on the thickness of the clay, its hardness, the character of the roof and floor, and the way in which it must be mined.

HAULAGE OF RAW MATERIALS TO FACTORY.

There are various methods that may be used in transporting the raw materials to the factory and the one to be adopted will depend upon the distance the material is to be transported, the amount to be conveyed, and the character of the country.

These various means of transporting the raw materials may be separated into the following groups:

Tramways, aerial cableways, transportation by water, transportation by steam or electric railways, and pumping.

TRAMWAYS.

Tramways are used where the material is to be transported short distances and are very satisfactory in such cases. Cable trams are especially well suited to handling materials over short distances and steep grades. Where a large amount of material is to be transported there should be an endless cable so that cars may be kept moving continually in one direction. In some cases gravity trams may be used to very great advantage, the loaded cars pulling up the empty ones. Locomotives propelled either by steam or electric power may be used where the distance is too great for cables.

AERIAL CABLEWAYS.

In many cases the aerial cableway furnishes a very satisfactory means of transporting cement materials from the deposits to the factory. They may be used with especial advantage where the country has a very rugged topography and where rivers and valleys are to be crossed. There are two general types of these aerial cableways. In one kind there is a single rope cable which supports and moves the load at the same time. In the other there are two or more large supporting cables and a small endless pulling rope. The large cable acts simply as a

track upon which the wheels of the buckets move. Beneath the large stationary cable is the small endless haulage cable to which the buckets are attached by means of friction grips. At one or both ends of the cableway are devices for loading and discharging the material, friction brakes, and driving gears. Supports of wood or steel are placed at intervals along the course of the cable. The buckets may hold from 500 to 1,600 pounds and have a speed of from 150 to 300 feet per minute. The double rope cableway is used much more than the single. They can be operated over longer distances and will handle more material in a given length of time. When properly installed they require but few repairs and furnish a very satisfactory means of transportation.

TRANSPORTATION BY WATER.

Water furnishes a very satisfactory means of transportation, especially where the distance the material has to be moved is great. Where good water transportation can be had it might be of advantage, in some cases at least, to locate the factory some distance from the raw material. Large quantities of material may be transported very cheaply on the water.

PUMPING.

Pumping is very little used in the transportation of raw cement materials. It is used only with marls and very soft clays. These are mixed with water and made up into a slurry and in this condition transported by pumping.

STEAM OR ELECTRIC RAILWAYS.

In some few cases it is found necessary to ship the raw materials for long distances over steam or electric railways. This means of transportation should not be used if it can possibly be avoided, as it is expensive and not very satisfactory from several standpoints.

CRUSHING OF THE RAW MATERIALS.

Soft materials like clay, chalk, and marl are readily broken up in the grinding of the mixture and hence, as a usual thing, require no preliminary crushing. In case they are crushed, however, rolls, disintegrators and machines of this type are

used. Hard materials, as limestone and shale, are put through a preliminary crusher, several types of which are in use, the jaw and the gyratory being the most common.

JAW CRUSHERS.

This type of crusher includes a number of makes, all of which act on the same principle. The Blake crusher is typical of the group. In this there is a vertical stationary jaw and a swinging apron jaw operated by an elliptical cam, giving it a forward and backward motion. The jaws are adjustable and the size of the crushed particles is determined by the size of the opening between the jaws at the lower ends. The opening between the jaws is greater at the upper ends than it is at the lower ends. As a piece of rock is seized by the jaw it is gradually crushed to a smaller and smaller size and worked down toward the lower end of the jaws or throat, as it is called, and finally passes out of the crusher. These jaws are made of very hard material, such as chrome or manganese steel, or chilled iron. The most essential qualifications for work of this kind is that the machine should be amply strong enough to withstand the greatest strains to which it is subjected. It should also be capable of taking large lumps and crushing them without their being broken with a sledge.

GYRATORY CRUSHERS.

The gyratory type of crusher is very popular for cement work. In these the crushing is continuous and is done by a gyrating vertical spindle, the upper end of which has the shape of a truncated cone. This spindle rotates within an inverted conical shell, the motion being imparted to it by bevel gears. When the machine is empty the spindle simply rotates and assumes the gyratory motion whenever rock is fed into it. This motion causes the head to approach and recede from the concave grinding surface of the shell which surrounds the cone, the movement at the bottom of the cone being greater than that at the top. The result is that there is a greater pressure, and hence crushing action, upon the smaller lumps at the bottom

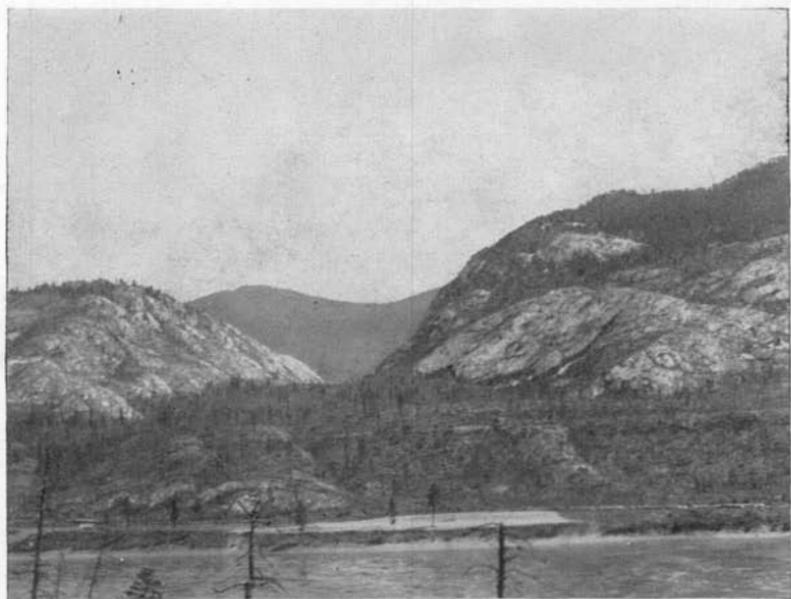
than upon the larger ones at the top. The size of the crushed product is regulated by the width of the throat at the bottom.

DRYING RAW MATERIALS.

After the materials have passed through the crushing or disintegration process, as the case may be, they must be dried before going on to the intermediate grinding. This is necessary because the raw materials as they come from the quarry, pit, or mine, will carry more or less water and this greatly reduces the efficiency of most modern types of grinding machinery and also tends to clog the discharge screens.

The percentage of water thus carried by the raw material will depend largely on the character of the material, method of handling and storing, and weather conditions. In the case of hard compact limestone freshly quarried, the amount is not large, usually being less than three per cent. In some cases these hard limestones are sent to the grinding mills without artificial drying. In the case of the soft chalky limestones, the amount is usually more and they must be put through driers. In all of these materials the water is simply held mechanically in the pores and is driven off at a comparatively low temperature.

With clays and shales, however, the case is quite different. Here there is, in addition to the hygroscopic or mechanically held water, also, always a certain amount of chemically combined water present. The amount of the mechanically held water will vary not only in the different clays, but also in the same clay under different conditions, and may range from as low as one to two per cent. in those clays that have been stored and air dried, to as high as thirty-four per cent. in some freshly dug clays. The amount of the chemically combined water will depend upon the composition of the clay and may vary from about five to ten per cent. The mechanically held water of a clay may be expelled at a temperature of from 100° to 110° C., but the chemically combined water is not lost until a low red heat is reached.



Limestone Bluffs along Columbia River, Stevens County.

The total amount of water then to be driven off from a clay may be from six to forty per cent. The average total amount of moisture, however, will probably be about sixteen or eighteen per cent. In the case of shales, while the water occurs mechanically held and chemically combined, there is usually less of it than there is in the clays. The total water in the shales will probably average about eight per cent.

Where the dry process of manufacture is in use it is necessary to remove practically all of this water before commencing the grinding of the materials. One reason for this is that fine grinding cannot be done economically or satisfactorily except on absolutely dry materials.

METHODS OF DRYING.

The type of dryer in most common use in cement plants consists of a cylinder from four to six feet in diameter and from forty to sixty feet in length, slightly inclined to the horizontal, and rotating on bearings. These cylinders are heated by a separate furnace at the lower end or by waste heat from the kilns. In either case the products of combustion enter at the lower end of the cylinder, are drawn through it, and pass out and escape through a stack at the upper end of the dryer. In many dryers angle irons are fastened to the inside of the cylinder in such a way that the material is lifted and dropped, in this way separating it more or less, and thus giving a better chance for the heat to come in contact with it and materially aiding in the drying process.

The dryer described above is the most simple and is very satisfactory for use on materials that have only small percentages of water. Where there is a large amount of water, however, in the materials, it seems that what are known as double heating dryers will prove much more satisfactory. What is known as the Ruggles-Coles dryer is a good example of this type. In this dryer two concentric hollow cylinders are employed and these are bolted together and rotated on an axis slightly inclined from the horizontal. The wet raw material is

fed into the space between the concentric cylinders, at the upper end of the dryer, and gradually works along between the cylinders down to the lower end of the dryer, where it is discharged. The heated gases pass through the inner cylinder from the upper to the lower end and through the space between the cylinders in the opposite direction. The material is thus being dried by the hot air and by coming in contact with the warmed outer surface of the inner cylinder.

The heat for this type of dryer may be direct heat, that is, heat from combustion especially intended for drying this material, or waste heat from the kilns. The waste heat dryers should be more economical than the others, as there is a saving of fuel and labor, because in the direct fired dryers the furnace requires stoking.

INTERMEDIATE GRINDING.

In the process of intermediate grinding, the material is usually reduced until it will pass about a thirty mesh screen. In some cases the raw materials pass this stage in reduction before they are mixed, but in others they are mixed in the proper proportions before the intermediate grinding is commenced.

MIXING THE RAW MATERIALS.

A thorough mixture of the raw materials is absolutely essential in order to produce a satisfactory cement, and the question of economy is the principal thing to be taken into consideration in determining whether the materials shall go through the process of intermediate grinding together or separately. In some cases the mixing is done after the intermediate grinding has been partly completed. The materials that are being mixed will also have something to do in determining the stage where this mixture should be made.

In the case of a limestone and clay mixture, where the limestone is not finely ground, there will be a tendency for the materials to separate and the mixture will not be a homogeneous one. If the limestone has been reduced to about the same condition as the clay, a much more homogeneous mixture will be obtained. The sampling and weighing of coarse material cannot

be so accurately or easily done as it can after the material is at least partially ground.

“At a number of plants the raw materials are mixed before or after being crushed, in such a manner that the composition is slightly higher in lime than is desired. This mixture is then passed through the ball mills, or other preliminary grinders, into steel bins holding several hours’ run. The material is automatically sampled as passed into the bins, and when the bin is filled, the sample is analyzed and the small amount of dried and ground shale or clay necessary to bring the mixture to the proper composition is then added. Three bins will be needed for the mixture and one for the shale.”*

The intermediate grinding of cement materials is being done by a number of different machines, the principle employed being somewhat different in different types. Most of these machines are capable of reducing the materials fine enough for burning, but some of them are considered to be not economical in the very fine grinding. The practice varies somewhat, but in general the materials are reduced in intermediate grinding so as to pass about twenty mesh.

The machines being used most extensively for the intermediate grinding of cement materials may be grouped into the following classes, according to their general methods of action: (1) Ball grinders; (2) centrifugal grinders; (3) rolls; (4) impact pulverizers.

BALL GRINDERS.

This class of grinders includes all those in which the raw material is ground by iron or steel balls rolling freely in a horizontal or slightly inclined revolving cylinder. The ball mill and the komminuter represent the principal types of this class. The ball mill consists of a cylindrical drum filled partly with steel balls. The inside lining consists of a series of steel steps which lap over on each other so when the drum revolves the balls, falling from one step to the other, crush the material. The crushed material drops through holes in the plates onto perforated steel screens which extend around the drum. The

*Meade, *Portland Cement*, 1911, p. 103.

first of these screens retains only the very coarsest particles, the finer falling onto another set of screens which separates the fully ground material from the coarse particles. In each case, the material that does not pass through the screens is returned to the inside of the drum.

The komminuter is a modification of the ball mill. It is about the same diameter as the ball mill but is about twice as long. It has the same arrangement of wrought iron or steel plates arranged in steps, as has the ball mill. Two sizes of screens surround the drum and tilt slightly toward the feed end of it. The material enters through an opening near the shaft and is ground by the balls as they fall from one grinding plate to another. The material gradually travels through the entire length of the drum to the lower end, where it is discharged onto the coarse screens. The material that will pass this screen drops down onto a finer one and the particles that do not pass it are returned automatically to the interior of the mill for finer grinding. The material passing the inside, or coarse screen, is caught on the outside or fine screen and further separated, the coarse particles being returned to the mill as before. These mills are said to have a greater capacity per horse power than the ordinary ball mill.

CENTRIFUGAL GRINDERS.

The most typical of this class of mills consist of a horizontal die ring and one or more vertically hung rollers. These rollers are held against this ring by centrifugal force and the material is ground between the rollers and the ring. Good examples of this class of grinders are the Griffin and the Huntington mills.

The Griffin mill consists of a horizontal pulley for receiving the power for operating it. From this pulley is suspended the shaft by means of a universal joint. To the lower end of this shaft is attached the crushing roll, which is free to swing in any direction in the case. The case consists of the base or pan containing the ring or die, against which the roll works and upon the inner vertical surface of which the pulverizing is done. In

dry pulverizing this pan or base has a number of openings through it downward outside of the ring or die, which lead into a pit from which the material is taken by a conveyer.

The material to be ground is subjected to two direct actions on account of the roll revolving in the opposite direction from that in which it travels around the die.

The Huntington mill acts on the same principle as the Griffin mill. It consists of three heavy rollers suspended in such a manner as to give them a free radial swing. When the head is revolved rapidly these rollers are thrown out against an enclosing die ring, due to centrifugal force. In this type of mill the individual rollers are not positively rotated by power applied directly to the upper end.

ROLLS.

Rolls are but little used in cement plants for grinding the raw materials. They are often used, however, as first reducers on clinker because they can handle hot clinker with less injury than any other form of grinding machinery. Where coal is used for burning the cement, rolls are very commonly used for crushing it.

IMPACT PULVERIZERS.

These machines reduce the material by direct blows struck by revolving bars or hammers. This type of pulverizer is most effective on soft materials and is often used on clay, shale and sometimes on very soft limestone.

FINE GRINDING.

For the fine grinding of raw materials used in the manufacture of Portland cement, practically all plants are supplied with either Griffin or tube mills, and as the Griffin mill has been described already, it only remains to give a brief description of the tube mill.

TUBE MILL.

This mill consists primarily of a long revolving cylinder of steel provided with a lining of suitable material to form an inner abrasive surface and to protect the outer shell from wear. The ends of the cylinder are closed by heavily reinforced cast

the different substances in it. Nevertheless, formulas have been proposed at different times by Le Chatelier, Newberry and others, by which to calculate mixtures of cement materials.

In the case of new and untried materials, it is necessary to rely entirely on the chemical analyses, and formulas enable us to arrive at a close approximation of the ultimate composition of Portland cement. The formula $3 \text{ CaO}, \text{ SiO}_2 + 2 \text{ CaO}, \text{ Al}_2\text{O}_3$, proposed by Professor Newberry, has been used extensively in the proportioning of raw materials. In this formula one part of silica corresponds by weight to five parts of calcium carbonate, and one part of alumina to two parts of calcium carbonate. In the calculation, the percentage of iron oxide is added to the percentage of alumina, the total being considered as alumina.

The following example shows the method of using this formula in the proportioning of a cement mixture:

ANALYSES OF RAW MATERIALS FROM BOSSBURG, STEVENS COUNTY.

CONSTITUENTS.	Limestone.	Clay.
Silica (SiO_2)	0.86	60.14
Alumina (Al_2O_3)	} 0.26	20.00
Iron (Fe_2O_3)		5.68
Lime (CaO)	54.86	4.07
Magnesia (MgO)	0.96	2.85
Alkalies ($\text{K}_2\text{O}, \text{Na}_2\text{O}$)	undt.
Loss on ignition.....	42.50	4.50
Total.....	99.44	97.24
Calcium carbonate (CaCO_3).....	97.65	7.27

This clay requires, according to the formula:

Parts of Clay.	Ration of CaCO_3 .	CaCO_3 Required.
Silica (SiO_2)	$60.14 \times 5 =$	300.70
Alumina (Al_2O_3)	$20.00 \times 2 =$	40.00
Iron (Fe_2O_3)	$5.68 \times 2 =$	11.36
		352.06
Calcium carbonate (CaCO_3).....		7.27
		344.79

The limestone contains small amounts of silica, alumina, and iron, and a small part of the lime in it will be required to satisfy these constituents:

Parts of Limestone.		
Silica (SiO_2)	$0.86 \times 5 =$	4.30
Alumina (Al_2O_3) }	$0.26 \times 2 =$	0.52
Iron (Fe_2O_3) }		
		4.82

iron heads, which have at their centers hollow trunions, through which the material is fed into the mill at one end and discharged at the other. The cylinder is partially filled with flint pebbles. The rotation of the cylinder carries the pebbles and the material being ground to a certain height within the mill, from which the mass falls, and in falling the pebbles are in constant action against each other and between them the material is ground by attrition.

These mills vary in size and are from 16 to 22 feet long and from 4 to 5 feet in diameter. The pebbles used in these mills are mostly imported from Greenland. They are put into the mill through a manhole and a screen is attached to the opening at the exit end of the mill to prevent their escape. The tube is lined with stone, silex, ironite, or cast iron. The silex lining is a very hard abrasive rock quarried in Europe. It is furnished in bricks of about four inches in width, eight inches in length, and from two and one-half to six inches in thickness. The ironite lining is similar to the silex but is made from a trap rock found in the United States. The cast iron lining is made of a special mixture of hard iron.

PROPORTIONING OF THE RAW MIXTURE.

A glance at the table of analyses of American Portland cements on page 79, will show a wide variation in chemical composition of this material. In proportioning the raw materials, however, no such latitude is allowed. The proper ratio must exist between the silica and alumina on the one hand and these and the lime on the other.

Many attempts have been made to put the calculation of cement mixtures on a scientific basis. If the theories of Le Chatelier and Newberry are taken as the basis, and Portland cement considered as composed of definite chemical compounds, then it becomes a comparatively easy matter and is simply a question of molecular or combining weights. Our knowledge, at the present time, however, as regards the composition of Portland cement, is very unsatisfactory, and it is impossible to express scientifically in mathematical formulas, the proportions of

This subtracted from the total CaCO_3 , leaves 92.83 parts of CaCO_3 in each unit of limestone and, as 344.79 parts of CaCO_3 are required for each unit of clay, the units of limestone required per unit of clay will be:

$$\frac{344.79}{92.83} = 3.82$$

In other words, 3.82 tons of limestone are required for each ton of clay.

In practice, the full amount of lime called for in Professor Newberry's formula is never employed, the percentage in all cases depending upon the fineness to which the raw materials are ground and the degree of burning. Usually about 90 per cent. of the lime called for by the formula is employed, or 4.5 is used instead of 5 as the factor for the silica, and 1.8 instead of 2 as the factor for the alumina and the iron.

Eckel* presents a formula which differs from Newberry's only in the fact that it takes into account the iron and the magnesia. The different steps in the process following this rule are given below:

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

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

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

*Cements, Limes, and Plasters, pp. 392-393.



General View of the Plant of the International Portland Cement Company, near Spokane.

Example: Given materials of the following composition the operation would be as follows:*

CONSTITUENTS.	Clay.	Limestone.
Silica (SiO ₂)	57.68	0.96
Alumina (Al ₂ O ₃)	22.60	0.20
Iron (Fe ₂ O ₃)	8.26
Lime (CaO)	5.95	55.10
Magnesia (MgO)	2.08	0.36
Alkalies (K ₂ O, Na ₂ O)	undt.
Loss on ignition.....	1.69	43.28
Total.....	98.26	99.90

Operation (1). Clay.

Silica	57.68 × 2.8 =	161.50
Alumina	22.60 × 1.1 =	24.86
Iron	8.26 × 0.7 =	5.78

192.34

Lime	5.95 × 1.0 =	5.95
Magnesia	2.08 × 1.4 =	2.91

8.86

$$192.34 - 8.86 = 183.48 = n$$

Operation (2). Limestone.

Silica	0.96 × 2.8 =	2.69
Alumina	0.20 × 1.1 =	2.20

4.89

Lime	55.10 × 1.0 =	55.10
Magnesia	0.36 × 1.4 =	0.50

55.61

$$55.61 - 4.89 = 50.72 = m$$

Operation (3).

$$\frac{n}{m} = \frac{183.48}{50.72} = 3.62$$

For each part of clay, by weight, 3.62 parts of limestone should be used. This, however, represents the very highest amount of lime theoretically possible under the most favorable conditions of fine grinding and thorough burning. These conditions in actual practice are never reached and it is customary to make a reduction of about 10 per cent. which in this case would leave 3.25 parts of limestone to one part of clay.

*Limestone and clay from Evans, Stevens County, Washington.

Most American Portland cements satisfy the formula (Michaelis' "hydraulic modulus"):

$$\frac{\% \text{ lime}}{\% \text{ silica} + \% \text{ iron oxide} + \% \text{ alumina}} = 1.8 \text{ to } 2.2$$

Meade,* in his work, found that where the raw materials were ground to a fineness so that 95% would pass through a No. 100 test sieve, that it was always possible to make a sound cement of normal setting properties and good strength when the composition of this cement met the ratio expressed by the following formula and provided the ratio between the silica and the alumina was not less than 2.5 to 1 nor more than 5 to 1:

$$\frac{\% \text{ lime}}{\% \text{ silica} - \% \text{ iron oxide} - \% \text{ alumina}} = 2.05$$

In actual mill practice it is very seldom that a ratio as high as this can be carried and just what the ratio should be will depend upon the character of the materials and conditions of manufacture. If the alumina is low the ratio may be carried as low as 1.9 without obtaining a quick setting cement. If, on the other hand, the alumina is high it may be necessary to carry the ratio as high as 2.05 to avoid a quick setting cement.

The formula used to proportion the raw materials so as to give a cement having a ratio of 2.05, is as follows:

$$\frac{\text{Limestone (or marl)}}{\text{Clay (or shale or cement rock)}} = \frac{(\% \text{ SiO}_2 + \% \text{ Fe}_2\text{O}_3 + \% \text{ Al}_2\text{O}_3 \text{ in clay}) \times 2\frac{1}{4} - (\% \text{ CaO in clay})}{(\text{CaO in limestone}) - (\% \text{ SiO}_2 + \% \text{ Fe}_2\text{O}_3 + \% \text{ Al}_2\text{O}_3 \text{ in limestone}) \times 2\frac{1}{4}}$$

The addition of 0.2 to 2.05 to give the 2 $\frac{1}{4}$ in the formula, is to take care of the small amount of coal ash which enters the cement.

As an example of the use of this formula, suppose we wish to calculate the proper mixture of limestone and clay having the composition shown by the above analyses of those from Evans, Stevens county.

$$\frac{\text{Limestone}}{\text{Clay}} = \frac{(62.20 + 22.60 + 8.26) \times 2\frac{1}{4} - 5.95}{55.10 - (0.96 + 0.20) \times 2\frac{1}{4}} = \frac{193.26}{52.49} = 3.68$$

*Portland Cement, p. 71.

The formulas given above are very valuable in determining the relative parts, by weight, of limestone and clay, or shale or cement rock, entering into a Portland cement mixture, but after a plant is in operation and running on materials of fairly uniform composition, it is customary to control the mixture according to a fixed lime standard. If, for instance, it is found that 42 per cent. lime (CaO) in the mixture of raw materials gave the best results, the mixtures would be made on this basis. In order to do this, however, the ratio of silica to alumina must remain fairly constant in the clay or shale.

After it has once been determined what amount of limestone and clay or shale, mixed together, give the best results, the mixture of raw materials may be calculated and controlled according to the percentage of lime (CaO) in the mixture according to the following simple algebraical method:*

Where x = weight of limestone in charge.

y = weight of clay or shale in charge.

a = per cent. of calcium oxide in limestone.

b = per cent. of calcium oxide in clay.

c = per cent. of calcium oxide in mixture.

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

The problem of determining the probable composition of a cement from its raw materials is often presented and its solution is by no means easy. The usual rule is to add together the percentage of silica, oxide of iron and alumina, lime and magnesia, and to divide this sum into the percentage of each compound, multiplied by 100, for the percentage of that compound which will be present in the clinker. If this rule is followed, the results obtained for silica and for iron oxide and alumina, will be too low and the lime much too high. This is because the ash of the fuel enters into the clinker, and also because the clinker contains other constituents present in the raw materials and not entirely volatilized in burning, viz., soda, potash, sulphur trioxide, carbon dioxide and water.

The accurate calculation of the composition of the clinker

*Ohio Geological Survey, Bulletin 3, 4th Series, p. 242.

$$ax + by = c(x + y)$$

from a chemical analysis of the raw material is, therefore, impossible and all that can be done is to assume certain corrections.

The following is from Portland Cement, by R. K. Meade, pp. 92-93, and shows the corrections made and the rule for calculating clinker from the analysis of the raw mixture:

The first correction is for the coal ash entering into the clinker, and Meade states that his "experiments show that in the rotary kiln about one-half the ash enters the clinker. The West Virginia gas slack coal contains about 10 per cent. ash on the average. This ash is composed of about 40 per cent. silica and about 20 per cent. each of iron oxide and alumina. If, therefore, 90 pounds of coal are required to burn a barrel of cement about 15 pounds (equivalent to 1.5 pounds of ash) are required per 100 pounds of raw material burned. Assuming half the ash to enter the raw material, the silica in the latter is increased by $\frac{1}{2} \times 1.5 \times 0.40 = 0.30$ per cent., and the iron and alumina each by $\frac{1}{2} \times 1.5 \times 0.20 = 0.15$ per cent."

"Analyses of Lehigh Valley clinker, when fresh from the kilns, show it to contain about 2 per cent. of potash, soda, sulphur compounds, carbon dioxide and water combined. Clinker from other localities will probably not vary very widely from this."

Making the above corrections, Meade's rule for calculating clinker from the mix analyses is as follows:

"Add together the percentages of silica, oxide of iron, alumina, lime and magnesia. To the sum add 2.75. Call the result the 'clinker total.'

"To find the percentage of silica, add 0.30 to the percentage of silica in the raw material, multiply the sum by 100 and divide by the 'clinker total' as found above. The result will be the percentage of silica in the clinker."

To find the percentage of iron oxide and alumina, add 0.30 to the sum of the iron and alumina in the mix, multiply by 100 and divide by "clinker total." The result will be the iron oxide plus the alumina in the clinker.

To find percentage of lime or magnesia, divide percentage of these by "clinker total" and multiply result by 100.

EXAMPLE. ANALYSIS OF RAW MATERIAL.

Silica (SiO_2)	13.44
Alumina (Al_2O_3) }	6.54
Iron (Fe_2O_3) }	
Lime (CaO)	41.84
Magnesia (MgO)	1.93

Total.....	63.75
Correction for ash, etc.....	2.75

Clinker total..... 66.50

Percentage of silica:

$$100 \times \frac{13.44 + 0.30}{66.50} = 20.66$$

Percentage of alumina and iron oxide:

$$100 \times \frac{6.54 + 0.30}{66.50} = 10.29$$

Percentage of lime:

$$\frac{100 \times 41.84}{66.50} = 62.92$$

Percentage of magnesia:

$$\frac{100 \times 1.93}{66.50} = 2.90$$

Probable composition of clinker:

Silica (SiO_2)	20.66
Alumina (Al_2O_3) }	10.29
Iron (Fe_2O_3) }	
Lime (CaO)	62.92
Magnesia (MgO)	2.90

BURNING THE MIXTURE.

After the raw materials have been carefully prepared and mixed as described in the preceding pages, the mixture must be burned with equal care.

In the early days of the industry a simple upright or dome kiln was used, the raw material being moulded into bricks and put into the kiln with alternate layers of coke. The daily output of this type of kiln is necessarily small and the expense for labor high. Improvements were made from time to time in this type of kiln and in localities where labor is very cheap this form of kiln is still used for burning Portland cement mixtures. In America, where labor is expensive and fuel comparatively

cheap, an entirely different style of kiln has been evolved and is used almost exclusively. This is the rotary kiln.

The rotary kiln, in its natural form, is a steel cylinder about six to nine feet in diameter and its length for dry materials ranges from sixty to one hundred and sixty feet. It is made of steel sheets from one-half to nine-sixteenths inches in thickness, and is lined with fire brick. In most cases the cylinders are the same diameter for the entire length, but in some cases the cylinder tapers for the last ten or fifteen feet before entering the stack. In still others, the cylinder is made of uniform diameter for the first forty feet and then tapers through about ten feet and then is of uniform diameter for the rest of its length.

This cylinder is set in a slightly inclined position, the inclination being about one-half inch to the foot and supported on two or more tires made of rolled steel and having a face of from six to twelve inches. The kiln is rotated by a girth gear, situated usually near its middle, and a train of gears, actuated either by line shaft or motor.

The upper end of the kiln projects into a flue which is surmounted by a steel stack while the lower end is closed by a hood into which the kiln projects. In some cases this hood is made stationary with removable doors, but usually it is mounted on a movable carriage. Two holes are usually left through the front wall of this hood. Through one of these the burning apparatus is inserted while the other is mainly for observing the operation of the kiln. The lower part of this hood is left partly open and through this the clinker falls and air for combustion enters.

The cement mixture is fed in at the upper end of the kiln, while fuel is supplied at the lower end. The fuel used varies in different localities and may be either powdered coal, oil or gas. The rotation of the kiln in connection with the inclination at which the cylinder is set, gradually carries the cement mixture to the lower end of the kiln. In the course of this journey, the intense heat generated by the burning fuel first drives off the water and carbon dioxide from the mixture, and then causes a chemical union of the lime, silica, alumina, and iron. This par-

tially fused mass forms what is known as "cement clinker." This clinker drops out of the lower end of the kiln at a temperature of about 2,000 degrees F., and must be cooled before it is sent to the grinding mills. The clinker is cooled mechanically or by allowing it to lie in heaps and cool of itself. Most plants, however, use some sort of mechanical contrivance for cooling the clinker, after which it is allowed to lie in a long pile in the open air for two or three weeks and season before it is ground.

GRINDING THE CLINKER.

The cement produced by the rotary kiln is so quick setting that some substance must be added to cause it to set more slowly. Gypsum is in general use for this purpose, and is added in quantities up to two and one-half to three per cent. In most cases the gypsum is added before the clinker is ground so as to secure thorough mixing of the gypsum with the cement.

In grinding the clinker, both intermediate and fine grinding mills are required. The intermediate grinder may be rolls, Kent mill, disintegrator, or ball-mill, while the fine grinders may be Griffin mills or tube mills. In many cases the same type of machinery is used in grinding the clinker that is used in the grinding of the raw material. The principal reason for this is that only one set of repair parts has to be carried in stock.

The tendency among engineers, at present, is to demand more finely ground cement. Comparative tests of finely and coarsely ground cements show results in favor of the more finely ground. An increase in the fineness by grinding, however, means a decrease in the amount produced per hour by the grinding mills employed, and consequently an increase in the cost of the cement, and at some point in the process the added cost would probably more than counterbalance the increase in strength due to very fine grinding.

The increase in the required fineness has been gradual, but quite 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., and a few very important specifications now require 95 per cent. to pass.